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THORPE'S DICTIONARY
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THORPE'S DICTIONARY
OF
APPLIED CHEMISTRY

BY
(*the late*)
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AND

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ASSISTED BY EMINENT CONTRIBUTORS

FOURTH EDITION (Revised and Enlarged)

VOL. V

WITH ILLUSTRATIONS

LONGMANS, GREEN AND CO.
LONDON ◆ NEW YORK ◆ TORONTO

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OF PATERNOSTER ROW
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LONGMANS, GREEN AND CO.
55 FIFTH AVENUE, NEW YORK
221 EAST 20TH STREET, CHICAGO
LONGMANS, GREEN AND CO.
215 VICTORIA STREET, TORONTO

FOURTH EDITION . . . 1941

CODE NUMBER: 96255

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Printed in Great Britain by William Clowes & Sons, Limited, Beccles

FOREWORD.

The death of Sir Jocelyn Thorpe on June 10, 1940, the day of publication of Volume IV of the Dictionary, not only removed from the Chemical world one of its most distinguished members, but also created a vacancy in the Editorship of the Dictionary that will not easily be filled. Happily the planning of the work was so far advanced that the publication of Volume V has presented no insuperable difficulties, although, owing to the war activities of some of the contributors, certain subjects which normally would have been treated here will appear under modified titles in subsequent volumes.

Gratitude is due to the Publishers not only for giving us priority of publication in spite of the difficulties due to war conditions, but also enabling us to issue with the volume an abridged interim index, in pamphlet form, to the first five volumes. This is a list of cross references occurring under other headings which would have appeared as separate entries in these and later volumes had the Dictionary been published as a complete work.

To our Reader, Dr. J. N. Goldsmith, we owe sincere thanks for his continued valuable assistance with the proofs and for many useful suggestions. We wish also to express our appreciation of the care and skill exhibited by the printers and draughtsmen in the setting up of this volume.

When, owing to war conditions, the work of the Dictionary could no longer be carried on in London it was transferred to the University Chemical Laboratory, Cambridge, where a room and library facilities were afforded by the Management Committee, to whom grateful acknowledgment is made.

M. A. WHITELEY.

CAMBRIDGE,
July, 1941.

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J. W. WOOD, *see* H. J. Hodsman.

ABBREVIATIONS

OF THE TITLES OF JOURNALS

A. I; *A.* II; *A.* III	British Chemical and Physiological Abstracts.
Acta Bot. Fennica	Acta Botanica Fennica.
Acta Physicochim. U.R.S.S.	Acta Physicochimica U.R.S.S.
Acta Phytochim.	Acta Phytochimica.
Acta Sci. Fennicæ	Acta Societatis Scientiarum Fennicæ.
Agric. Eng.	Agricultural Engineering.
Agric. Gaz. New South Wales	Agricultural Gazette of New South Wales.
Agric. J. Brit. Guiana	Agricultural Journal of British Guiana.
Agric. Live-stock India	Agriculture and Live-stock in India.
Allgem. Oel- Fett-Ztg.	Allgemeine Oel- und Fett-Zeitung.
Allgem. Z. Bierbrau.	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation.
Aluminium	Aluminium.
Amer. Chem. Abstr.	Chemical Abstracts. Published by the American Chemical Society.
Amer. Dyestuff Rep.	American Dyestuff Reporter.
Amer. Gas J.	American Gas Journal.
Amer. Inst. Min. Met. Eng. Publ.	American Institute of Mining and Metallurgical Engineers Technical Publications, New York.
Amer. J. Bot.	American Journal of Botany.
Amer. J. Dis. Child.	American Journal of Diseases of Children.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Publ. Health	American Journal of Public Health and The Nation's Health.
Amer. J. Sci.	American Journal of Science.
Amer. Min.	American Mineralogist.
Amer. Paint J.	American Paint Journal.
Anal. Asoc. Quím. Argentina	Anales de la Asociación Química Argentina.
Anal. Fís. Quím.	Anales de la Sociedad Española de Física y Química.
Analyst	Analyst.
Angew. Bot.	Angewandte Botanik.
Angew. Chem.	Angewandte Chemie (*changed from* Z. angew. Chem. *in 1932*).
Ann. Acad. Sci. Fennicæ	Annales Academiæ Scientiarum Fennicæ.
Ann. agron.	Annales agronomiques.
Ann. Appl. Biol.	Annals of Applied Biology.
Ann. Bot.	Annals of Botany.
Ann. Chim.	Annales de Chimie.
Ann. Chim. Analyt.	Annales de Chimie Analytique et de Chimie Appliquée.
Ann. Chim. Farm.	Annali di Chimica Farmaceutica.
Ann. di Bot.	Annali di Botanica.
Ann. Falsif.	Annales des Falsifications et des Fraudes.
Ann. Ferm.	Annales des Fermentations.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Inst. Platine	Annales de l'Institut du Platine et des autres Métaux Précieux, U.S.S.R.
Ann. Mines	Annales des Mines (Paris).
Ann. Mines Belg.	Annales des Mines de Belgique.
Ann. Off. nat. Comb. liq.	Annales de l'Office national des Combustibles liquides.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. R. Staz. Chim. Agrar. Sperim.	Annali della R. Stazione Chimico-Agraria Sperimentale di Roma.
Ann. Sci.	Annals of Science.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Ann. Sect. Anal. phys. chim.	Annales du Secteur d'Analyse Physico-chimique, Inst. de chemie générale, U.S.S.R.

Ann. Soc. Sci. Bruxelles	Annales de la Société Scientifique de Bruxelles.
Annalen	Justus Liebig's Annalen der Chemie.
Annali Chim. Appl.	Annali di Chimica Applicata.
Arbeitsphysiol.	Arbeitsphysiologie.
Arch. Biol.	Archives de Biologie.
Arch. Eisenhüttenw.	Archiv für das Eisenhüttenwesen.
Arch. exp. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Farm. sperim.	Archivio di Farmacologia sperimentale e Scienze affini.
Arch. Gewerbepath. Gewerbehyg.	Archiv für Gewerbepathologie und Gewerbehygiene.
Arch. Hyg. Bakt.	Archiv für Hygiene und Bakteriologie.
Arch. int. Physiol.	Archives internationales de Physiologie.
Arch. intern. Med.	Archives of Internal Medicine.
Arch. Ist. Biochim. Ital.	Archivio dello Istituto Biochimico Italiano.
Arch. Mikrobiol.	Archiv für Mikrobiologie.
Arch. Min. Soc. Sci. Varsovie	Archives de Minéralogie de la Société des Sciences de Varsovie (Archivum Mineralogiczne Towarzystwa Naukowego Warszawskiego).
Arch. Néerland.	Archives Néerlandaises des sciences exactes et naturelles.
Arch. Néerland. Physiol.	Archives Néerlandaises de Physiologie de l'Homme et des Animaux.
Arch. Pflanzenbau	Archiv für Pflanzenbau.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arch. Suikerind. Ned.-Indië	Archief voor de Suikerindustrie in Nederlandsch-Indië.
Arch. Tierernährung u. Tierzucht	Archiv für Tierernährung und Tierzucht.
Arch. Wärmewirts.	Archiv für Wärmewirtschaft.
Arizona Agric. Exp. Sta. Bull.	Arizona Agricultural Experiment Station Bulletin.
Arkiv Kemi, Min., Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Astrophys. J.	Astrophysical Journal.
Atti R. Accad. Lincei	Atti della Reale Accademia Nazionale dei Lincei.
Atti R. Accad. Sci. Torino	Atti della Reale Accademia delle Scienze di Torino.
Austral. J. Exp. Biol.	Australian Journal of Experimental Biology and Medicine.
B.	British Chemical Abstracts. B.—Applied Chemistry.
B.P.	British Patent.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Ber. deut. bot. Ges.	Berichte der deutschen botanischen Gesellschaft.
Ber. Ges. Kohlentech.	Berichte der Gesellschaft für Kohlentechnik.
Ber. Sächs. Akad. Wiss.	Berichte über die Verhandlungen der Sächsischen Akademie der Wissenschaften zu Leipzig.
Ber. Ukrain. Wiss. Forsch. physikal. Chem.	Berichte des Ukrainischen Wissenschaftlichen Forschungsinstituts für physikalische Chemie.
Berlin. klin. Woch.	Berliner klinische Wochenschrift.
Bied. Zentr.	Biedermann's Zentralblatt Abt. A. für Agrikulturchemie.
Bied. Zentr. (Tierernähr.)	Biedermann's Zentralblatt Abt. B. Tierernährung.
Biochem. J.	Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Biochimia	Biochimia, U.S.S.R.
Bodenk. Pflanzenernähr.	Bodenkunde und Pflanzenernährung.
Bol. Acad. Nac. Ciencias, Cordoba	Boletín de la Academia Nacíonal des Ciencias, Córdoba.
Bol. Soc. Quim. Peru	Boletin de la Sociedad Quimica del Peru.
Boll. Chim. farm.	Bollettino Chimico Farmaceutico.
Boll. Sez. Ital.	Bollettino della Sezione Italiana, Società internazionale di microbiologia.
Boll. Soc. Geol. Ital.	Bollettino della Società Geologica Italiana.
Boll. Soc. Ital. Biol. sperim.	Bollettino della Società Italiana di Biologia Sperimentale.
Boll. Uff. Staz. Sperim. Ind. Essenze	Bollettino Ufficiale della R. Stazione Sperimentale per l'Industria delle Essenze e dei Derivati dagli Agrumi in Reggio Calabria.
Bot. Archiv	Botanisches Archiv.
Bot. Gaz.	Botanical Gazette.
Brass. Malt.	Brasserie et Malterie.
Brau- u. Malzind.	Brau- u. Malzindustrie.
Braunkohle	Braunkohle.
Braunkohlenarchiv	Braunkohlenarchiv.
Brennstoff-Chem.	Brennstoff-Chemie.
Brewers' J.	Brewers' Journal.
Brit. Dental J.	British Dental Journal.

Brit. Guiana Dept. Agric. Bull.	British Guiana Department of Agriculture, Bulletin.
Brit. J. Exp. Path.	British Journal of Experimental Pathology.
Brit. J. Phot.	British Journal of Photography.
Brit. J. Phys. Med.	British Journal of Physical Medicine.
Brit. Med. J.	British Medical Journal.
Brit. Plastics	British Plastics and Moulded Products Trader.
Bul. Chim. Soc. Române	Buletinul de Chimie Pură şi Aplicată al Societătii Române de Chemie.
Bul. Soc. Fiz. România	Buletinul Bilunar al Societătii de Fizică din România.
Bull. Acad. Méd. Roumanie	Bulletin de l'Académie de Médecine de Roumanie.
Bull. Acad. Polonaise	Bulletin International de l'Académie Polonaise des Sciences et des Lettres.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Agra & Oudh	Bulletin of the Academy of Sciences of the United Provinces of Agra and Oudh.
Bull. Acad. Sci. Roumaine	Bulletin de la Section Scientifique de l'Académie Roumaine.
Bull. Acad. Sci. U.R.S.S.	Bulletin de l'Académie des Sciences de l'Union des Républiques Soviétiques Socialistes.
Bull. Agric. Chem. Soc. Japan	Bulletin of the Agricultural Chemical Society of Japan.
Bull. Amer. Ceram. Soc	Bulletin of the American Ceramic Society.
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.
Bull. Biol. Méd. exp. U.R.S.S.	Bulletin de Biologie et Médecine expérimentale de l'U.R.S.S.
Bull. Chem. Soc. Japan	Bulletin of the Chemical Society of Japan.
Bull. Dept. Agric. Kenya	Bulletin of the Department of Agriculture of Kenya Colony.
Bull. Dept. Agric. S. Africa	Bulletin of the Department of Agriculture of South Africa.
Bull. Entomol. Res.	Bulletin of Entomological Research.
Bull. Forest Exp. Stat. Meguro	Bulletin of the Forest Experiment Station, Meguro, Tokyo.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Inst. Min. Met.	Bulletin of the Institution of Mining and Metallurgy.
Bull. Inst. Phys. Chem. Res. Japan	Bulletin of the Institute of Physical and Chemical Research, Japan (Rikwagaku Kenkyujo Ihō).
Bull. Inst. Pin	Bulletin de l'Institut du Pin.
Bull. Johns Hopkins Hosp.	Bulletin of the Johns Hopkins Hospital.
Bull. Mat. Grasses	Bulletin des Matières Grasses.
Bull. Photogrammétrie	Bulletin de Photogrammétrie.
Bull. Rubber Growers' Assoc.	Bulletin of the Rubber Growers' Association.
Bull. School Mines and Met., Univ. Missouri	Bulletin of the School of Mines and Metallurgy, University of Missouri, Columbia.
Bull. Sci. pharmacol.	Bulletin des Sciences pharmacologiques.
Bull. Sericult. Japan	Bulletin of Sericulture and Silk Industry, Japan.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol.	Bulletin de la Société de Chimie biologique.
Bull. Soc. Chim. Yougoslav.	Bulletin de la Société Chimique du Royaume de Yougoslavie.
Bull. Soc. Franç. Min.	Bulletin de la Société Française de Minéralogie.
Bull. Soc. Franç. Phot.	Bulletin de la Société Française de Photographie et de Cinématographie.
Bull. Soc. Ind. Mulhouse	Bulletin de la Société Industrielle de Mulhouse.
Bull. Soc. Sci. Hyg. aliment.	Bulletin de la Société Scientifique d'Hygiène alimentaire.
Bull. U.S. Geol. Survey	Bulletin of the U.S. Geological Survey.
Canad. Chem.	Canadian Chemistry and Process Industries.
Canad. Dairy & Ice Cream J.	Canadian Dairy and Ice Cream Journal.
Canad. J. Res.	Canadian Journal of Research.
Canada Dept. Mines Publ.	Canada Department of Mines Publications.
Caoutchouc et Gutta-Percha	Le Caoutchouc et la Gutta-Percha.
Cellulose-chem.	Cellulosechemie.
Cement and Lime Manuf.	Cement and Lime Manufacture.
Centr. Zuckerind.	Centralblatt fur die Zuckerindustrie.
Cereal Chem.	Cereal Chemistry.
Chem. Age	Chemical Age.
Chem. and Ind.	Chemistry and Industry.
Chem. App.	Chemische Apparatur.
Chem. Eng. Min. Rev.	Chemical Engineering and Mining Review.
Chem. Erde	Chemie der Erde.
Chem. Fabr.	Chemische Fabrik.
Chem. Ind.	Chemische Industrie.

Chem. Listy	Chemické Listy pro Vědu a Průmysl. Organ de la "Ceská chemická Společnost pro Vedu a Průmysl."
Chem. Met. Eng.	Chemical and Metallurgical Engineering.
Chem. Obzor.	Chemický Obzor.
Chem. Soc. Annual Rep.	Annual Reports on the Progress of Chemistry, issued by the Chemical Society.
Chem. Social. Agric.	Chemisation of Socialistic Agriculture (U.S.S.R.).
Chem. Trade J.	Chemical Trade Journal.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zentr.	Chemisches Zentralblatt.
Chem.-Ztg.	Chemiker-Zeitung.
Cheshunt Agric. Exp. Sta. Ann. Rep.	Cheshunt Experimental and Research Station, Annual Report.
Chim. e L'Ind.	La Chimica e L'Industria.
Chim. et Ind.	Chimie et Industrie.
Chinese J. Physics	Chinese Journal of Physics.
Chinese J. Physiol.	Chinese Journal of Physiology, Pekin.
Coal Age	Coal Age.
Coal Carbonisation	Coal Carbonisation.
Coll. Czech Chem. Comm.	Collection of Czech Chemical Communications.
Coll. Eng.	Colliery Engineering.
Coll. Guard.	Colliery Guardian.
Collegium	Collegium.
Colorado Agric. Exp. Sta. Bull.	State Agricultural College of Colorado, Agricultural Experiment Station, Fort Collins, Bulletin.
Combustion	Combustion.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Acad. Agric. France	Comptes rendus hebdomadaires des Séances de l'Académie d'Agriculture de France.
Compt. rend. Acad. Sci. U.R.S.S.	Comptes rendus de l'Académie des Sciences de l'U.R.S.S.
Compt. rend. Soc. Biol.	Comptes rendus des Séances de la Société de Biologie.
Compt. rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux du Laboratoire Carlsberg.
Cornell Univ. Agric. Exp. Sta. Bull.	Cornell University College of Agriculture, New York, Agricultural Experiment Station, Bulletin.
Current Sci.	Current Science.
Cyprus Agric. J.	Cyprus Agricultural Department, Journal.
Dairy Ind.	Dairy Industry.
Dansk Tidsskr. Farm.	Dansk Tidsskrift for Farmaci.
Delaware Agric. Exp. Sta. Bull.	University of Delaware, Newark Agricultural Experiment Station, Bulletin.
Dept. Chem. S. Australia, Bull.	Department of Chemistry, South Australia, Bulletins.
Deut. Apoth.-Ztg.	Deutsche Apotheker-Zeitung (*changed from* Apotheker-Zeitung *in 1934*).
Deut. med. Woch.	Deutsche medizinische Wochenschrift.
Deut. Zuckerind.	Deutsche Zuckerindustrie.
Dinglers Polytech. J.	Dinglers Polytechnisches Journal.
East Malling Res. Sta., Ann. Repts., etc.	East Malling Research Station, Annual Reports, etc.
Econ. Proc. Roy. Dubl. Soc.	Economic Proceedings of the Royal Dublin Society.
Empire Cotton Growing Rep. Exp. Sta.	Empire Cotton Growing Reports of the Experimental Station.
Empire Cotton Growing Rev.	Empire Cotton Growing Review.
Empire J. Exp. Agric.	Empire Journal of Experimental Agriculture.
Eng. and Min. J.	Engineering and Mining Journal.
Ergebn. Physiol.	Ergebnisse der Physiologie.
Ernähr. Pflanze	Ernährung der Pflanze, Deutsches Kalisyndikat.
Ernährung	Die Ernährung, Deutsche Gesellschaft für Ernährungsforschung.
F.P.	French Patent.
Facts about Sugar	Facts about Sugar.
Farbe u. Lack	Farbe und Lack.
Farben-Chem.	Farben-Chemiker.
Farben-Ztg.	Farben-Zeitung.
Färber-Ztg.	Deutsche Färber-Zeitung.
Fermentforsch.	Fermentforschung.
Fert. Feeding Stuffs J.	Fertiliser, Feeding Stuffs and Farm Supplies Journal.
Fette u. Seifen	Fette und Seifen.

Feuerungstech.	Feuerungstechnik.
Finska Kem. Medd.	Finska Kemistsamfundets Meddelanden (Suomen Kemistiseuran Tiedonantoja).
Florida Agric. Exp. Sta. Bull.	University of Florida, Gainsville Agricultural Experiment Station, Bulletin.
Food Manuf.	Food Manufacture.
Food Res.	Food Research, Champaign, Illinois.
Foundry Trade J.	Foundry Trade Journal.
Fruit Prod. J.	Fruit Products Journal.
Fuel	Fuel in Science and Practice.
Fuel Econ.	Fuel Economist.
Fuel Econ. Rev.	Fuel Economy Review.
G.P.	German Patent.
Gas Age-Rec.	Gas Age-Record.
Gas Ind.	Gas Industry (*discontinued 1936*).
Gas J.	Gas Journal.
Gas Times	Gas Times.
Gas- u. Wasserfach	Gas- und Wasserfach.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Georgia Agric. Exp. Sta. Bull.	Georgia Experiment Station Athens, Georgia, U.S.A., Bulletin.
Ges. Abh. Kennt. Kohle	Gesammelte Abhandlungen zur Kenntnis der Kohle.
Glass Ind.	Glass Industry.
Glashütte	Die Glashütte.
Gummi-Ztg.	Gummi-Zeitung.
Hawaii Agric. Exp. Stat. Bull.	Hawaii Experiment Station Bulletins, Hawaiian Sugar Planters Association, Honolulu.
Helv. Chim. Acta	Helvetica Chimica Acta.
Imp. Bur. Soil Sci. Tech. Comm.	Imperial Bureau of Soil Science, Technical Communications, Harpenden.
Ind. Chem.	Industrial Chemist.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
Ind Eng. Chem. [Anal.]	Industrial and Engineering Chemistry, Analytical Edition.
Indian J. Agric. Sci.	Indian Journal of Agricultural Science.
Indian J. Med. Res.	Indian Journal of Medical Research.
Indian J. Physics	Indian Journal of Physics.
Indian J. Vet. Sci.	Indian Journal of Veterinary Science.
Indian Lac Res. Inst. Bull.	Indian Lac Research Institute Bulletin.
India-Rubber J.	India-Rubber Journal.
Int. Rev. Agric.	International Review of Agriculture.
Int. Sugar J.	International Sugar Journal.
Iron Age	Iron Age.
Iron Steel Inst. Carnegie Schol. Mem.	Iron and Steel Institute, Carnegie Scholarship Memoirs.
J.C.S.	Journal of the Chemical Society.
J.S.C.I.	Journal of the Society of Chemical Industry.
J. Agric. Chem. Soc. Japan	Journal of the Agricultural Chemical Society of Japan.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Ceram. Soc.	Journal of the American Ceramic Society.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Leather Chem. Assoc.	Journal of the American Leather Chemists' Association.
J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association.
J. Amer. Soc. Agron.	Journal of the American Society of Agronomy.
J. Amer. Soc. Mech. Eng.	Journal of the American Society of Mechanical Engineers.
J. Amer. Water Works Assoc.	Journal of the American Water Works Association.
J. Appl. Chem. U.S.S.R.	Journal of Applied Chemistry, U.S.S.R.
J. Appl. Physics	Journal of Applied Physics (*formerly* Physics).
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
J. Austral. Inst. Agric. Sci.	Journal of the Australian Institute of Agricultural Science.
J. Bact.	Journal of Bacteriology.
J. Biochem. Japan	Journal of Biochemistry, Japan.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Brit. Dairy Farmers' Assoc.	Journal of the British Dairy Farmers' Association.
J. Brit. Wood Pres. Assoc.	Journal of the British Wood Preserving Association.
J. Cellulose Inst. Tokyo	Cellulose Industry, Journal of the Cellulose Institute, Tokyo.

J. Chem. Educ.	Journal of Chemical Education.
J. Chem. Eng. China	Journal of Chemical Engineering, China.
J. Chem. Ind. U.S.S.R.	Journal of Chemical Industry, U.S.S.R.
J. Chem. Met. Soc. S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
J. Chem. Physics	Journal of Chemical Physics.
J. Chem. Soc. Japan	Journal of the Chemical Society of Japan. (Nippon Kwagaku Kwaishi.)
J. Chim. phys.	Journal de Chimie physique.
J. Chinese Chem. Soc.	Journal of the Chinese Chemical Society.
J. Coll. Agric. Hokkaido	Journal of the College of Agriculture, Hokkaido Imperial University, Japan.
J. Coll. Agric. Tokyo	Journal of the College of Agriculture, Imperial University of Tokyo, Japan.
J. Coll. Eng. Tokyo	Journal of the College of Engineering, Imperial University of Tokyo.
J. Counc. Sci. Ind. Res. Australia	Journal of the Council of Scientific and Industrial Research of Australia.
J. Dairy Res.	Journal of Dairy Research.
J. Dairy Sci.	Journal of Dairy Science.
J. Dept. Agric. I.F.S.	Journal of the Department of Agriculture of the Irish Free State.
J. Dept. Agric. Kyushu	Journal of the Department of Agriculture, Kyushu Imperial University.
J. Dept. Agric. S. Australia	Journal of the Department of Agriculture, South Australia.
J. Dept. Agric. Victoria	Journal of the Department of Agriculture, Victoria.
J. Dept. Agric. W. Australia	Journal of the Department of Agriculture, Western Australia.
J. Econ. Entomol.	Journal of Economic Entomology.
J. Egypt. Med. Assoc.	Journal of the Egyptian Medical Association.
J. Electrodep. Tech. Soc.	Journal of the Electrodepositors' Technical Society.
J. Exp. Biol.	Journal of Experimental Biology.
J. Exp. Med.	Journal of Experimental Medicine.
J. Faculty Sci. Tokyo	Journal of the Faculty of Science, Imperial University of Tokyo.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Fuel Soc. Japan	Journal of the Fuel Society of Japan.
J. Gen. Chem. U.S.S.R.	Journal of General Chemistry, U.S.S.R. (*formerly part of* J. Russ. Phys. Chem. Soc.).
J. Gen. Physiol.	Journal of General Physiology.
J. Geol.	Journal of Geology.
J. Geol. Soc. Tokyo	Journal of the Geological Society of Tokyo.
J. Hygiene	Journal of Hygiene.
J. Ind. Hyg.	Journal of Industrial Hygiene and Toxicology.
J. Indian Chem. Soc.	Journal of the Indian Chemical Society.
J. Indian Inst. Sci.	Journal of the Indian Institute of Science.
J. Inst. Brew.	Journal of the Institute of Brewing.
J. Inst. Fuel	Journal of the Institute of Fuel.
J. Inst. Metals	Journal of the Institute of Metals.
J. Inst. Petroleum Tech.	Journal of the Institution of Petroleum Technologists.
J. Inst. Sewage Purif.	Journal of the Institute of Sewage Purification.
J. Iron and Steel Inst.	Journal of the Iron and Steel Institute.
J. Jap. Ceram. Assoc.	Journal of the Japanese Ceramic Association.
J. Landw.	Journal für Landwirtschaft.
J. Marine Biol. Assoc.	Journal of the Marine Biological Association of the United Kingdom.
J. Med. Res.	Journal of Medical Research.
J. Min. Agric.	Journal of the Ministry of Agriculture.
J. Min. Agric. N. Ireland	Journal of the Ministry of Agriculture of Northern Ireland.
J. New England Water Works Assoc.	Journal of the New England Water Works Association.
J. Nutrition	Journal of Nutrition.
J. Oil Col. Chem. Assoc.	Journal of the Oil and Colour Chemists' Association.
J. Opt. Soc. Amer.	Journal of the Optical Society of America.
J. Org. Chem.	Journal of Organic Chemistry.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Exp. Ther.	Journal of Pharmacology and Experimental Therapeutics.
J. Pharm. Soc. Japan	Journal of the Pharmaceutical Society of Japan. (Yakugakuzasshi.)
J. Phys. Chem. U.S.S.R.	Zhurnal Fizicheskoi Khimii (*formerly part of the* Journal of the Russian Physical-Chemistry Society).
J. Phys. Radium	Journal de Physique et Le Radium.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.

J. Physiol. Path. gén.	Journal de Physiologie et de Pathologie générale.
J. Pomology	Journal of Pomology and Horticultural Science.
J. pr. Chem.	Journal für praktische Chemie.
J. Proc. Asiatic Soc. Bengal	Journal and Proceedings of the Asiatic Society of Bengal.
J. Proc. Austral. Chem. Inst.	Journal and Proceedings of the Australian Chemical Institute.
J. Proc. Roy. Soc. New South Wales	Journal and Proceedings of the Royal Society of New South Wales.
J. Res. Nat. Bur. Stand.	Journal of Research of the National Bureau of Standards.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Hort. Soc.	Journal of the Royal Horticultural Society.
J. Roy. Microscop. Soc.	Journal of the Royal Microscopical Society.
J. Roy. Soc. W. Australia	Journal of the Royal Society of Western Australia.
J. Roy. Tech. Coll.	Journal of the Royal Technical College (Glasgow).
J. Rubber Res.	Journal of Rubber Research.
J. Rubber Res. Inst. Malaya	Journal of the Rubber Research Institute of Malaya.
J. S. African Chem. Inst.	Journal of the South African Chemical Institute.
J. Sci. Hiroshima Univ.	Journal of Science of the Hiroshima University.
J. Sci. Instr.	Journal of Scientific Instruments.
J. Sci. Tech. India	Journal of Science and Technology, India.
J. Scot. Met. Soc.	Journal of the Scottish Meteorological Society.
J. Soc. Arts	Journal of the Royal Society of Arts.
J. Soc. Chem. Ind. Japan	Journal of the Society of Chemical Industry, Japan. (Kōgyō Kwagaku Zasshi.)
J. Soc. Dyers and Col.	Journal of the Society of Dyers and Colourists.
J. Soc. Glass Tech.	Journal of the Society of Glass Technology.
J. Soc. Leather Trades' Chem.	Journal of the International Society of Leather Trades' Chemists.
J. South-East. Agric. Coll.	Journal of the South-Eastern Agricultural College, Wye, Kent.
J. State Med.	Journal of State Medicine.
J. Text. Inst.	Journal of the Textile Institute.
J. Univ. Bombay	Journal of the University of Bombay.
J. Usines Gaz	Journal des Usines à Gaz.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
J. West Scotland Iron Steel Inst.	Journal of the West of Scotland Iron and Steel Institute.
Jahrb. geol. Reichsanst.	Jahrbuch der geologischen Reichsanstalt.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie; Beilage Band.
Jahrb. Radioaktiv.	Jahrbuch der Radioaktivität und Elektronik.
Jahrb. wiss. Bot.	Jahrbuch für wissenschaftliche Botanik.
Jahresber.	Jahresberichte über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften.
Japan. J. Med. Sci.	Japanese Journal of Medical Sciences.
Japan. J. Physics	Japanese Journal of Physics.
Japan Nickel Rev.	Japan Nickel Review.
Kali	Kali, verwandte Salze und Erdoel.
Kentucky Agric. Exp. Stat. Bull.	University of Kentucky Agricultural Experiment Station, Lexington, Bulletin.
Keram. Rundsch.	Keramische Rundschau.
Klin. Woch.	Klinische Wochenschrift.
Kolloid-Beih.	Kolloid-Beihefte.
Kolloid. Shurn.	Kolloidnyi Zhurnal (Colloid Journal, U.S.S.R.).
Kolloid-Z.	Kolloid-Zeitschrift.
Lait	Le Lait.
Lancet	The Lancet.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
London Shellac Res. Bur., Tech. Paper	London Shellac Research Bureau, Technical Paper.
Malay. Agric. J.	Malayan Agricultural Journal.
Mass. Agric. Exp. Sta. Bull.	Massachusetts Agricultural Experiment Station, Bulletin.
Materie Plast.	Materie Plastiche.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden från Kungl-Vetenskapsakademiens Nobel Institut.
Mem. Accad. Lincei	Memorie della Reale Accademia Nazionale dei Lincei.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Agric. Kyoto	Memoirs of the College of Agriculture, Kyoto Imperial University.
Mem. Coll. Sci. Kyoto	Memoirs of the College of Science, Kyoto Imperial University.
Mem. Dept. Agric. India	Memoirs of the Department of Agriculture in India (*discontinued 1930*).

Mem. Inst. Chem. Ukrain. Acad. Sci.	Memoirs of the Institute of Chemistry, Ukrainian Academy of Sciences.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mém. Poudres	Mémorial des Poudres.
Mém. Soc. Ing. Civ. France	Mémoires et Compte rendu des Travaux de la Société des Ingénieurs Civils de France.
Met. & Alloys	Metals and Alloys.
Met. Clean. and Fin.	Metal Cleaning and Finishing.
Metal Ind. (Lond.)	Metal Industry.
Metal Ind. (N.Y.)	Metal Industry (New York).
Metal Progr.	Metal Progress.
Metall u. Erz	Metall und Erz.
Metallges. Rev.	Metallgesellschaft Periodic Review.
Metallurgia	Metallurgia.
Metals Tech.	Metals Technology.
Metrop. Water Bd. Rep.	Metropolitan Water Board Reports.
Mich. Agric. Exp. Sta. Bull.	Michigan State College Agricultural Experiment Station Lansing, Bulletin.
Mikrochem.	Mikrochemie.
Milch. Forsch.	Milchwirtschaftliche Forschungen.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Milk Ind.	Milk Industry.
Milk Plant Month.	Milk Plant Monthly.
Min. & Met.	Mining and Metallurgy.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Missouri Agric. Exp. Sta. Res. Bull.	University of Missouri Agricultural Experiment Station Columbia, Research Bulletin.
Mitt. Kohlenforschungsinst. Prag	Mitteilungen des Kohlenforschungsinstituts in Prag.
Mitt. Lebensm. Hyg.	Mitteilungen aus dem Gebiete der Lebensmitteluntersuchungen und Hygiene.
Mitt. Materialprüf.	Mitteilungen aus dem Materialprüfungsamt zu Berlin-Dahlem.
Mitt. med. Ges. Tokyo	Mitteilungen der medizinischen Gesellschaft zu Tokyo.
Mitt. Path. Inst. K. Univ. Japan	Mitteilungen aus dem pathologischen Institut der Kaiserlichen Universität zu Sendai, Japan.
Mitt. Textilforsch. Krefeld	Mitteilungen der Textilforschungsanstalt, Krefeld e.V.
Monatsh.	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Monit. Sci.	Moniteur Scientific (from 1927 merged in La Revue de Chimie industrielle).
Montana Agric. Exp. Sta. Bull.	Montana Agricultural Experiment Station Bulletin.
Month. J. Inst. Metals	Monthly Journal of the Institute of Metals.
Month. Rep. Dept. Agric. N. Ireland.	Monthly Reports of the Department of Agriculture of Northern Ireland.
Mühlenlab.	Das Mühlenlaboratorium.
Münch. med. Woch.	Münchener medizinische Wochenschrift.
Nachr. Ges. Wiss. Göttingen	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Nat. Butter & Cheese J.	National Butter and Cheese Journal.
Nat. Paint Var. Assoc. Circ.	National Paint, Varnish, and Lacquer Association, Inc., Circular.
Naturwiss.	Die Naturwissenschaften.
Natuurwetensch. Tijds.	Natuurwetenschappelijk Tijdschrift.
New Hamps. Agric. Exp. Sta. Bull.	New Hampshire Agricultural Experiment Station Bulletin.
New Jersey Agric. Exp. Sta. Bull.	New Jersey, New Brunswick Agricultural Experiment Station, Bulletin.
New Phytol.	New Phytologist.
New York Agr. Expt. Sta. Bull.	New York State Department of Agriculture, Bulletins.
New York (Geneva) Agric. Exp. Sta. Bull.	New York (Geneva) Agricultural Experiment Station, Bulletin.
New Zealand Dominion Laby. Rept.	New Zealand Dominion Laboratory Reports.
New Zealand J. Sci. Tech.	New Zealand Journal of Science and Technology.
Nova Acta Soc. Sci.	Nova Acta Regiae Societatis Scientiarum Upsaliensis.
Nutr. Abs.	Nutrition Abstracts and Reviews.
Öfvers. Finska Vet.-Soc.	Öfversigt af Finska Vetenskaps-Societétens Förhandlingar, Helsingfors.
Oel u. Kohle	Oel und Kohle.

Off. Digest	Official Digest of the Federation of Paint and Varnish Production Clubs.
Ohio Agric. Exp. Sta. Bull.	Ohio Agricultural Experiment Station Bulletin.
Oil and Gas J.	Oil and Gas Journal.
Oklahoma Agric. Exp. Sta. Bull.	Oklahoma Agricultural Experiment Station Bulletin.
Öle, Fette, Wächse	Öle, Fette, Wächse, Seife, Kosmetik.
Österr. Chem.-Ztg.	Österreichische Chemiker-Zeitung.
Oversigt Danske Vid. Selsk.	Oversigt over det Kongelige Danske Videnskabernes Selskabs Virksomhed.
Pacific Pulp and Paper Ind.	Pacific Pulp and Paper Industry.
Paint and Var. Prod. Man.	Paint and Varnish Production Manager.
Paint Manuf.	Paint Manufacture.
Paint, Oil, and Chem. Rev.	Paint, Oil, and Chemical Review.
Paint Tech.	Paint Technology.
Paper Ind.	Paper Industry.
Paper-Maker	Paper-Maker and British Paper Trade Journal.
Paper Trade J.	Paper Trade Journal.
Papier-Fabr.	Papier-Fabrikant.
Peint., Pig., Ver.	Peintures, Pigments, Vernis.
Perf. & Essent. Oil Rec.	Perfumery and Essential Oil Record.
Petroleum	Petroleum (Vienna).
Pflügers Archiv	Archiv für die gesamte Physiologie des Menschen und der Tiere.
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zentralh.	Pharmazeutische Zentralhalle.
Pharm. Ztg.	Pharmazeutische Zeitung.
Philippine Agric.	Philippine Agriculturist.
Philippine J. Sci.	Philippine Journal of Science.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phot. Ind.	Photographische Industrie.
Phot. J.	Photographic Journal.
Phot. Korr.	Photographische Korrespondenz.
Physica	Physica.
Physical Rev.	Physical Review.
Physics	Physics (*now* Journal of Applied Physics).
Physikal. Z.	Physikalische Zeitschrift.
Physikal. Z. Sovietunion	Physikalische Zeitschrift der Sovietunion.
Plant Physiol.	Plant Physiology.
Planta (Z. wiss. Biol.)	Planta (Zeitschrift für wissenschaftliche Biologie).
Plast. Massi	Plastitschekie Massi (*in 1935 merged in* Organic Chemical Industry, U.S.S.R.).
Poultry Sci.	Poultry Science Association, U.S.A.
Proc. Acad. Sci. Agra and Oudh	Proceedings of the Academy of Sciences of the United Provinces of Agra and Oudh, India.
Proc. Amer. Acad. Arts Sci.	Proceedings of the American Academy of Arts and Sciences.
Proc. Amer. Gas Assoc.	Proceedings of the American Gas Association.
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Amer. Soc. Biol. Chem.	Proceedings of the American Society of Biological Chemists.
Proc. Amer. Soc. Test. Mat.	Proceedings of the American Society for Testing Materials.
Proc. Austral. Inst. Min. Met.	Proceedings of the Australasian Institute of Mining and Metallurgy.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Chem. Eng. Group	Proceedings of the Chemical Engineering Group of the Society of Chemical Industry.
Proc. Durham Phil. Soc.	Proceedings of the University of Durham Philosophical Society.
Proc. Eng. Soc. W. Pa.	Proceedings of the Engineers' Society of Western Pennsylvania.
Proc. Imp. Acad. Tokyo	Proceedings of the Imperial Academy, Tokyo.
Proc. Indian Acad. Sci.	Proceedings of the Indian Academy of Sciences.
Proc. Inst. Mech. Eng.	Proceedings of the Institution of Mechanical Engineers.
Proc. Internat. Cong. Soil Sci.	Proceedings of the International Congress of Soil Science.
Proc. Internat. Soc. Soil Sci.	Proceedings of the International Society of Soil Science.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Leningrad Dept. Inst. Fert.	Proceedings of the Leningrad Departmental Institute of Fertilisers.

Proc. Muslim Assoc.	Proceedings of the Muslim Association for the Advancement of Science.
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Nova Scotian Inst. Sci.	Proceedings of the Nova Scotian Institute of Science.
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Inst.	Proceedings of the Royal Institution of Great Britain.
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Proc. Roy. Soc. Med.	Proceedings of the Royal Society of Medicine.
Proc. Roy. Soc. Queensland	Proceedings of the Royal Society of Queensland.
Proc. Roy. Soc. Tasmania	Proceedings of the Royal Society of Tasmania.
Proc. S. Wales Inst. Eng.	Proceedings of the South Wales Institute of Engineers.
Proc. Sci. Assoc., Vizianagram	Proceedings of the Science Association, Maharajah's College, Vizianagram.
Proc. Soc. Biol. Chem. India	Proceedings of the Society of Biological Chemists, India.
Proc. Tech. Sect. Paper Makers' Assoc.	Proceedings of the Technical Section of the Paper Makers' Association of Great Britain and Ireland.
Proc. U.S. Nat. Mus.	Proceedings of the United States National Museum.
Przemysl Chem.	Przemysł Chemiczny.
Publ. Fac. Sci. Univ. Masaryk	Publications de la Faculté des Sciences de l'Université Masaryk (Spisy vydávané Přírodovědeckou Fakultou Masarykovy University).
Pulp and Paper Mag. Canada	Pulp and Paper Magazine of Canada.
Quart. J. Exp. Physiol.	Quarterly Journal of Experimental Physiology.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Quart. J. Med.	Quarterly Journal of Medicine.
Quart. J. Pharm.	Quarterly Journal of Pharmacy and Pharmacology.
Queensland J. Agric.	Queensland Agricultural Journal.
Rayon Text. Month.	Rayon Textile Monthly.
Rec. Australian Mus.	Records of the Australian Museum.
Rec. trav. bot. Néerland.	Recueil des travaux botaniques Néerlandaises.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas.
Refiner	Refiner and Natural Gasoline Manufacturer.
Rend. Accad. Sci. Fis. Mat. Napoli	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
Rend. Ist. Lomb. Sci. Lett.	Rendiconti della Reale Istituto Lombardo di Scienze e Lettere.
Rensselaer Polyt. Inst. Bull.	Rensselaer Polytechnic Institute Bulletin.
Rep. Aust. Assoc. Sci.	Reports of the Australasian Association for the Advancement of Science.
Rep. Brit. Assoc.	Reports of the British Association for the Advancement of Science.
Res. Stud. State Coll. Washington	Research Studies of the State College of Washington.
Rev. Aluminium	Revue de l'Aluminium.
Rev. Chim. Ind.	Revista de Chimica Industrial.
Rev. Chim. pura appl.	Revista de Chimica pura e applicada, Ôrgão de Sociedade Portuguêsa de Química e Física.
Rev. Comb. liq.	Revue des Combustibles liquides.
Rev. Fac. Quim. Ind. Agric.	Revista de la Facultad de Química Industrial y Agrícola.
Rev. Gén. Mat. Col.	Revue Générale des Matières Colorantes.
Rev. Mét.	Revue de Métallurgie.
Rev. Mod. Physics	Review of Modern Physics.
Rev. Quim. Farm.	Revista de Química e Farmacia.
Rev. Sci. Instr.	Review of Scientific Instruments.
Rocz. Chem.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
Rubber Chem. & Tech.	Rubber Chemistry and Technology.
Sborn. Trud. Ukrain. Chim. Inst. Odessa	Sbornik Trudov Ukrainskogo Nautschno-Issledova-Telskogo Chimitscheskogo Instituta Odessa.
Sci. Agric.	Scientific Agriculture.
Sci. and Cult.	Science and Culture.
Sci. Ind. Rep. Roure-Bertrand Fils	Scientific and Industrial Reports of Roure-Bertrand Fils.
Sci. Mem. Univ. Saratov	Scientific Memoirs of the University of Saratov.
Sci. Papers Inst. Phys. Chem. Res. Tokyo	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Proc. Roy. Dublin Soc.	Scientific Proceedings of the Royal Dublin Society.

Sci. Quart. Nat. Univ. Peking	Science Quarterly of the National University of Peking.
Sci. Rep. Hiroshima Tech. Sch.	Scientific Reports of the Hiroshima Higher Technical School.
Sci. Rep. Tôhoku	Science Reports, Tôhoku Imperial University.
Sci. Rep. Tsing Hua Univ.	Science Reports of the National Tsing Hua University.
Sci. Sect. Nat. Paint, Var. Assoc. Circ.	Scientific Section, National Paint, Varnish, and Lacquer Association, Inc., Circulars.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Scot. J. Agric.	Scottish Journal of Agriculture.
Seifens.-Ztg.	Seifensieder-Zeitung.
Sewage Works J.	Sewage Works Journal.
Sitzungsber. Akad. Wiss. Wien	Sitzungsberichte der Akademie der Wissenschaften in Wien.
Sitzungsber. Heidelberger Akad. Wiss.	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Smithsonian Misc. Coll.	Smithsonian Miscellaneous Collections.
Soap	Soap.
Soap Trade Rev.	Soap, Perfumery and Cosmetics.
Soil Res.	Soil Research.
Soil Sci.	Soil Science.
Sprechsaal	Sprechsaal für Keramik-Glas-Email. Fach- und Wirtschaftsblatt für die Silikat-Industrien.
Stahl u. Eisen	Stahl und Eisen.
Stain Tech.	Stain Technology.
Staz. sper. agr. ital.	Stazioni sperimentali agrarie italiane (*discontinued 1926*).
Steam Eng.	Steam Engineer.
Sugar Bull.	Sugar Bulletin.
Suomen Kem.	Suomen Kemistilehti (*formerly until* 1935 Acta Chemica Fennica).
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift.
Tasmanian Agric. J.	Tasmanian Journal of Agriculture.
Tech. Mitt. Krupp	Technische Mitteilungen Krupp.
Tech. Publ. Tin Res. Counc.	Technical Publications of the International Tin Research and Development Council.
Tech. Rep. Tôhoku	Technology Reports of the Tôhoku Imperial University, Sendai, Japan.
Teer u. Bitumen	Teer und Bitumen.
Tekn. Tidsk.	Teknisk Tidskrift.
Textilber.	Melliand's Textilberichte.
Tids. Kjemi	Tidsskrift for Kjemi og Bergvesen, Oslo.
Tonind.-Ztg.	Tonindustrie-Zeitung.
Trans. Amer. Inst. Chem. Eng.	Transactions of the American Institute of Chemical Engineers.
Trans. Amer. Inst. Metals	Transactions of the American Institution of Metals.
Trans. Amer. Inst. Min. Met. Eng.	Transactions of the American Institute of Mining and Metallurgical Engineers.
Trans. Amer. Soc. Mech. Eng.	Transactions of the American Society of Mechanical Engineers.
Trans. Amer. Soc. Met.	Transactions of the American Society of Metals.
Trans. Canad. Inst. Mining Met.	Transactions of the Canadian Institute of Mining and Metallurgy.
Trans. Ceram. Soc.	Transactions of the Ceramic Society.
Trans. Electrochem. Soc.	Transactions of the Electrochemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Inst. Min. Eng.	Transactions of the Institution of Mining Engineers.
Trans. Inst. Min. Met.	Transactions of the Institution of Mining and Metallurgy.
Trans. Inst. Plast. Ind.	Transactions of the Institute of the Plastics Industry.
Trans. Inst. Rubber Ind.	Transactions of the Institution of the Rubber Industry.
Trans. N. Eng. Inst. Min. Mech. Eng.	Transactions of the North of England Institute of Mining and Mechanical Engineers.
Trans. New Zealand Inst.	Transactions of the New Zealand Institute (*since 1934* Royal Society of New Zealand).
Trans. Nova Scotian Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin.	Transactions of the Royal Society of Edinburgh.
Trans. Roy. Soc. S. Africa	Transactions of the Royal Society of South Africa.

Trans. Saratov Univ.	Transactions of the Saratov University (Gelehrte Notizen der Saratover Staats-Universität).
Trop. Agric.	Tropical Agriculturist, Ceylon.
Trop. Agric. (Trinidad)	Tropical Agriculture (Trinidad).
Tsch. Min. Mitt.	Mineralogische und Petrographische Mitteilungen (Zeitschrift für Kristallographie, Mineralogie, und Petrographie, Abteilung B).
U.S. Bur. Mines, Bull., Tech. Papers, and Rept. Invest.	United States Bureau of Mines, Bulletins, Technical Papers, and Reports of Investigations.
U.S. Bur. Plant Ind.	United States Bureau of Plant Industry, Department of Agriculture.
U.S. Dept. Agric. Bull. (or *Circ.*)	United States Department of Agriculture, Bulletins (*or* Circulars).
U.S. Hyg. Labor. Bull.	United States Public Health Service, Hygienic Laboratory Bulletins.
U.S.P.	United States Patent.
U.S. Publ. Health Rep.	United States Public Health Reports.
Ukrain. Biochem. J.	Ukrainian Biochemical Journal.
Ukrain. Chem. J.	Ukrainian Chemical Journal.
Union S. Africa Dept. Agric. Bull.	Union of South Africa Department of Agriculture, Bulletins.
Univ. Illinois Bull.	University of Illinois Agricultural Experimental Station, Bulletin.
Utah Agric. Coll. Exp. Stat. Bull.	Utah State Agricultural College Experiment Station, Bulletin.
Verh. Geol. Reichsanst. Wien	Verhandlungen der Geologischen Bundesanstalt in Wien.
Verh. Ges. deut. Naturforsch. Aerzte	Verhandlungen der Gesellschaft deutscher Naturforscher und Aerzte.
Vermont Agric. Exp. Sta. Bull.	University and State of Vermont Agricultural Experiment Station, Bulletin.
Verre et Silicates Ind.	Verres et Silicates Industriels.
Vet. J.	Veterinary Journal.
Vet. Rec.	Veterinary Record.
Virginia (Blacksburg) Exp. Sta. Bull.	Virginia Polytechnic Institute, Blacksburg Experiment Station, Bulletin.
Welsh J. Agric.	Welsh Journal of Agriculture.
Wiss. Veröff. Siemens-Werken	Wissenschaftliche Veröffentlichungen aus den Siemens-Werken.
Woch. Brau.	Wochenschrift für Brauerei.
World's Paper Tr. Rev.	World's Paper Trade Review.
Z. angew. Chem.	Zeitschrift für angewandte Chemie (*in 1932 changed to* Angewandte Chemie).
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Biol.	Zeitschrift für Biologie.
Z. deut. Geol. Ges.	Zeitschrift der deutschen Geologischen Gesellschaft.
Z. Elektrochem.	Zeitschrift für Elektrochemie.
Z. Fleisch- Milch-Hyg.	Zeitschrift für Fleisch- und Milch-Hygiene.
Z. ges. Brauw.	Zeitschrift für das gesamte Brauwesen.
Z. ges. exp. Med.	Zeitschrift für die gesamte experimentelle Medizin.
Z. ges. Naturwiss.	Zeitschrift für die gesamte Naturwissenschaft.
Z. ges. Schiess- u. Sprengstoffw.	Zeitschrift für das gesamte Schiess- und Sprengstoffwesen.
Z. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten.
Z. Krist.	Zeitschrift für Kristallographie.
Z. Metallk.	Zeitschrift für Metallkunde.
Z. Parasitenk.	Zeitschrift für Parasitenkunde.
Z. Pflanz. Düng.	Zeitschrift für Pflanzenernährung, Düngung, und Bodenkunde (*title 1936 changed to* Bodenkunde und Pflanzenernährung).
Z. Pflanzenkr. Pflanzenschutz	Zeitschrift für Pflanzenkrankheiten (Pflanzenpathologie) und Pflanzenschutz.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem.	Zeitschrift für physikalische Chemie.
Z. physikal. chem. Unterr.	Zeitschrift für den physikalischen und chemischen Unterricht.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. pr. Geol.	Zeitschrift für praktische Geologie.
Z. Spiritusind.	Zeitschrift für Spiritusindustrie.
Z. Unters. Lebensm.	Zeitschrift für Untersuchung der Lebensmittel.
Z. Ver. deut. Ing.	Zeitschrift des Vereins deutscher Ingenieure.
Z. Ver. deut. Zucker-Ind.	Zeitschrift des Vereins der deutschen Zucker-Industrie (*in 1935 changed to* Zeitschrift der Wirtschaftsgruppe Zuckerindustrie).
Z. Vitaminforsch.	Zeitschrift für Vitaminforschung.

Z. Wirts. Zuckerind.	Zeitschrift der Wirtschaftsgruppe Zuckerindustrie (Verein der deutschen Zucker-Industrie).
Z. wiss. Biol.	Zeitschrift für wissenschaftliche Biologie.
Z. wiss. Mikrosk.	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.
Z. wiss. Phot.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Z. Züchtung	Zeitschrift für Züchtung, Reihe A Pflanzen-, Reihe B Thier-.
Z. Zuckerind. Czechoslov.	Zeitschrift für die Zuckerindustrie der Čechoslovakischen Republik.
Zellstoff u. Papier	Zellstoff und Papier.
Zement	Zement.
Zentr. Bakt.	Zentralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten. Abt. I and II.
Zentr. Min.	Zentralblatt für Mineralogie, Geologie und Paläontologie.

NOTE.

Italicised words in inverted commas may be registered trade names.

A DICTIONARY OF APPLIED CHEMISTRY

F—*continued.*

FEHLING'S SOLUTION *v.* Barreswil's Solution (Vol. I, 648*d*).

FEIGL'S TEST *v.* Arsenic (Vol. I, 471*c*).

FELDMANN STILL *v.* Ammonia (Vol. I, 345*b*).

FELITE *v.* Building Materials (Vol. II, 141*b*).

FELLIC ACID *v.* Bile (Vol. I, 690*a*).

FELSITE *v.* China-Stone (Vol. III, 32*d*).

FELSPAR or FELDSPAR. (Fr. *Feldspath*; Ger. *Feldspath, Feldspat*; from the Swedish *Feltspat* or *Fältspat,* meaning "field-spar.") The original form of the name, as given by D. Tilas in 1740, is *feldtspat* (N. Zenzén, Geol. För. Förh. Stockholm, 1925, **47,** 390). A large isomorphous group of important rock-forming minerals consisting of alumino-silicates of alkalis (potassium and sodium, rarely rubidium, cæsium and lithium) and alkaline earths (calcium, and less often barium). They include polysilicates or trisilicates of the type $R'AlSi_3O_8$, and orthosilicates of the type $R''Al_2(SiO_4)_2$. The principal molecules representing the end-members of the isomorphous series are $KAlSi_3O_8$ (Or=orthoclase), $NaAlSi_3O_8$ (Ab=albite), and $CaAl_2Si_2O_8$ (An=anorthite). Others of less importance, or whose existence is only assumed on theoretical grounds, are $BaAl_2Si_2O_8$ (Ce=celsian), $Na_2Al_2Si_2O_8$ (Cg =carnegieite), and $RbAlSi_3O_8$ (rubidium-microcline).

The felspars are divided crystallographically into two series, the monoclinic (or oblique) felspars and the triclinic (or anorthic) felspars. But, although these belong to different systems of crystallisation, they resemble one another closely in habit, cleavage, and general crystallographic characters. An important feature of all felspars is the existence of good cleavages in two directions; the more perfect one being parallel to the basal pinakoid *c*(001), whilst the second is parallel to the clinopinakoid or plane of symmetry *b*(010) in the monoclinic felspars, and parallel to the corresponding brachypinakoid *b*(010) in the triclinic felspars. In the monoclinic system these two cleavages are necessarily at right angles (90°), and the felspars belonging to this system are consequently described as orthoclastic felspars; whilst in the triclinic system the cleavage angle *bc* varies slightly from a right angle (in anorthite *bc*=85° 50′, and in albite *bc*=86° 24′), and for this reason these felspars are called plagioclastic felspars, or simply plagioclase. To these two series may be added a third—pseudo-monoclinic series—the members of which are shown by their optical characters to be triclinic, but in the external form of their crystals they do not differ from those of the monoclinic series and the cleavage angle *bc* does not differ appreciably from 90°. The several members of these three series of felspars are set out in the following table:—

	Monoclinic series.	Pseudo-monoclinic series.	Triclinic series.
$KAlSi_3O_8$	Orthoclase	Microcline	—
$mKAlSi_3O_8$ $nNaAlSi_3O_8$	Soda-orthoclase	Anorthoclase	—
$NaAlSi_3O_8$	Barbierite	Cryptoclase	Albite
$mNaAlSi_3O_8$ $nCaAl_2Si_2O_8$	—	—	Oligoclase, Labradorite, etc.
$CaAl_2Si_2O_8$	—	—	Anorthite
$Na_2Al_2Si_2O_8$	—	—	Carnegieite
$BaAl_2Si_2O_8$	Celsian	—	—
$mBaAl_2Si_2O_8$ $nKAlSi_3O_8$	Hyalophane	—	—

The only members of practical importance are the potash-felspars, orthoclase and microcline (which, as noted below, are perhaps really identical); the soda-felspar, albite; the lime-felspar, anorthite; and the soda-lime-felspars, oligoclase, andesine, labradorite and bytownite, All of these, with the exception of potash-felspar, belong to the isomorphous group of plagioclase-felspars of which albite and anorthite are the end-members. The limits of composition usually assigned to these are:

			SiO_2	Al_2O_3	Na_2O	CaO
Plagioclase-felspars.	Albite	Ab_1An_0	68·7	19·5	11·8	—
	Oligoclase	Ab_6An_1	64·9	22·1	10·0	3·0
	Andesine	Ab_3An_1	62·0	24·0	8·7	5·3
	Labradorite	Ab_1An_1	55·6	28·3	5·7	10·4
	Bytownite	Ab_1An_3	49·3	32·6	2·8	15·3
	Anorthite	Ab_1An_6	46·6	34·4	1·6	17·4
		Ab_0An_1	43·2	36·7	—	20·1

A character which always enables the plagioclase-felspars to be readily recognised is the invariable presence of lamellar twinning according to the albite-law. This is shown in thin sections of rocks when examined in polarised light by the banding due to the different directions of extinction in alternate lamellæ. In a hand-specimen it is shown on the basal plane *c*(001), and on the perfect cleavage parallel to this face, by a system of fine striæ parallel to the edge of intersection of the two cleavages. These striæ can usually be detected with the aid of a pocket-lens when the cleavage surface is held at a suitable inclination to the light; and two sets of reflections can be obtained in albite inclined at 7° 12′, and in anorthite at 8° 20′. Albite-twinning is not present in orthoclase, but is present in microcline, though in this case the striæ are not evident on the cleavage surface. This difference often affords a ready means of distinguishing at sight a potash-felspar from a soda-lime-felspar. In microcline there is also a second lamellar twinning according to the pericline-law, which, in conjunction with the lamellar albite-twinning, produces a very characteristic cross-hatched structure, sometimes to be seen on the basal plane of crystals, but very evident when thin sections are examined in polarised light; this being, indeed, often the only means of distinguishing microcline. Several other twin-laws have been described for the felspars, the important ones being the Carlsbad, Baveno and Manebach types. The very common occurrence of repeated twinning in this group of minerals gives rise to the suggestion that the higher degree of symmetry in the monoclinic series is merely the result of twinning, and that all felspars are really triclinic. This is obviously the case in the pseudo-monoclinic series, in which, on optical examination, the twinning is seen to be repeated on a very minute scale. If this became ultramicroscopic, then the crystal could not be distinguished from a true monoclinic crystal. The crystallographic grouping shown in the above table would then break down, while the chemical grouping would stand. Microcline would then be identical with orthoclase, which, indeed, it is in density, refractive indices, mode of occurrence and its practical applications.

Some of the constants of the three most important species of felspar are given in the table at the top of the next column.

	Orthoclase ($KAlSi_3O_8$)	Albite ($NaAlSi_3O_8$)	Anorthite ($CaAl_2Si_2O_8$)
SiO_2%	64·7	68·7	43·2
Al_2O_3%	18·4	19·5	36·7
CaO%	—	—	20·1
K_2O%	16·9	—	—
Na_2O%	—	11·8	—
Sp. gr.	2·56	2·62	2·76
Hardness	6–6½	6–6½	6–6½
Melting-point °C. .	*c.* 1150	*c.* 1100	1550
Specific heat . . .	0·187	0·197	0·197
Cleavage angle (*bc*) .	90°	86° 24′	85° 50′
Optical extinction on *c*	0°	+4°	−37°
,, ,, *b*	+5°	+19°	−36°
Ref. index (Na) α .	1·519	1·529	1·576
,, ,, β .	1·523	1·533	1·583
,, ,, γ .	1·524	1·539	1·588
Birefringence $\gamma - \alpha$.	0·005	0·010	0·012

The recognition of a mineral as felspar is usually evident by the cleavages, dullness of colour and lustre, hardness, resistance to acids, etc.; but the discrimination of the several species is not always so easy. The optical characters of cleavage flakes afford a useful guide, and the specific gravity of fragments can be readily determined in a heavy liquid with the aid of indicators. Optical methods, with the aid of the universal microscope stage, have been much developed (M. Reinhard, "Universal Drehtischmethoden . . . Plagioklasbestimmung," Basel, 1931; W. Nikitin, "Die Fedorow-Methode," Berlin, 1936). J. Szabo ("Ueber eine neue Methode die Feldspathe auch in Gesteinen zu bestimmen," Budapest, 1876; *v.* G. A. J. Cole, "Aids to Practical Geology," 5th ed., London 1906, 78–85) devised a method in which the intensity of coloration imparted to the Bunsen flame gives an approximate indication of the percentage of potassium and sodium present. Anorthite is decomposed by hydrochloric acid with separation of gelatinous silica. The other felspars are only very slightly attacked by acids (except hydrofluoric), alkaline solutions and carbonated water; but they are decomposed by hot alkaline solutions under pressure.

The following analyses are of: I, Orthoclase from Norway, as used in the manufacture of porcelain; formula $Or_{78}Ab_{22}$. II, Microcline (amazon-stone) from Antaboka, Madagascar, $Or_{71}Ab_{27}An_2$. III, Albite from Amelia Co., Virginia, $Ab_{98}Or_2$. IV, Oligoclase (sunstone) from Tvedestrand, Norway, $Ab_{71}An_{22}Or_7$. V, Labradorite from Ardglass, Co. Down, $Ab_{33}An_{62}Or_5$. VI, Anorthite from Vesuvius, $Ab_4An_{94}Or_2$.

	I	II	III	IV	V	VI
SiO_2 .	64·98	63·55	68·44	61·30	52·33	43·96
Al_2O_3 .	19·18	18·55	19·35	23·77	30·22	35·30
Fe_2O_3 .	0·33	0·34	—	0·36	0·40	0·63
CaO .	trace	0·36	—	4·87	12·52	18·98
MgO .	0·25	0·10	—	—	—	0·45
K_2O .	12·79	13·90	0·43	1·29	0·85	0·40
Na_2O .	2·32	3·30	11·67	8·50	3·62	0·47
Ign. .	0·48	—	—	—	0·36	—
	100·33	100·10	99·89	100·09	100·30	100·19
Sp. gr. .	—	2·58	2·61	2·66	2·71	2·76

Felspars are of wide distribution, according to F. W. Clarke forming about 56 p.c. of the earth's crust. They occur as primary constituents in igneous rocks of nearly all kinds, and are abundant in gneisses and metamorphic rocks. The alkali-felspars occur preferably in the more siliceous rocks (granite, etc.), whilst lime-felspars are more common in basic rocks (gabbro, basalt, etc.). Anorthite is also found in certain types of meteoric stones. Felspars are very susceptible to alteration, being attacked by carbonated, acid and alkaline waters, and they give rise to a great variety of secondary minerals. By the action of weathering processes the alkalis and lime generally pass into solution, remaining partly in the soil, and in part being removed in solution to form eventually secondary deposits of salts and limestone; whilst kaolin and free silica remain behind to give rise to deposits of clay.

All the naturally-occurring felspars have been prepared artificially, and in addition others containing strontium, barium and lead in place of calcium, or potassium in place of sodium in the plagioclases. The basic felspars crystallise readily and are easily obtained by dry fusion; but the alkali-felspars form extremely viscous glasses, and have not been crystallised by dry fusion without fluxes. Much experimental work has been done in connection with the isomorphism of the felspars and in rock synthesis (*v.* F. Fouqué and A. Michel-Lévy, " Synthèse des Minéraux et des Roches," Paris, 1882; A. L. Day and E. T. Allen, " The Isomorphism and Thermal Properties of the Feldspars," Carnegie Inst., Washington, 1905).

For practical purposes the felspars find applications in several directions. Some are used as gem-stones and ornamental stones. As a rule, these minerals are dull in colour, cloudy and imperfectly transparent, but certain varieties exhibit special optical and colour effects. *Moonstone,* a variety of orthoclase obtained mainly from Ceylon, displays a soft bluish milky sheen (glaucescence). Somewhat similar, but with brighter colours, is *peristerite* (named from *περιστερά*, a pigeon, on account of the colours resembling those on a pigeon's neck), a variety of albite from Canada. *Sunstone*, or avanturine felspar, exhibits a metallic spangled effect, due to the enclosure of scales of hæmatite; this is best shown in the oligoclase from Tvedestrand in Norway, but is also met with in some other felspars. *Labradorite* in certain specimens, particularly those found abundantly as boulders on the coast of Labrador, are of a dull dark-grey colour, yet at just a particular angle with respect to the incident light they suddenly shine up with brilliant metallic colours. This change of colour or labradorescence is due to the interference of light caused by numerous minute enclosures in the mineral. The same effect is also shown by the anorthoclase in the *augite-syenite* (laurvikite) from Laurvik and Fredriksvärn in the south of Norway, a rock much used as a polished ornamental stone. A clear transparent oligoclase from Mitchell Co., North Carolina, has been cut in the brilliant form as a gem. *Amazon-stone* (*q.v.*) is a green microcline. (On the use of felspar as gem-stones, *v.* M. Bauer, " Precious Stones," transl. by L. J. Spencer, London, 1904.)

The chief use of felspar in the industrial arts is for the manufacture of porcelain and enamel ware of all kinds, including electrical goods. For this purpose only an alkali-felspar, preferably potash-felspar or a potash-soda-felspar, is employed; the lime-felspars not being suitable, since they readily crystallise. In the finest porcelain, felspar (10–35%) is added to the body, and as it fuses it firmly binds the particles of clay and quartz; but it is chiefly for the glaze that felspar (30–50%) is added. The best quality is used for making artificial teeth. Small amounts are used by glass manufacturers, especially for producing an opalescent glass. Fused felspar forms a firm bond for emery, corundum and carborundum wheels.

As an abrasive, felspar is especially suitable for certain purposes. Owing to its cleavage, it powders to angular fragments; and its hardness is about the same as that of glass. It is therefore used as a cleaner and polisher of glass articles, and forms an ingredient of scouring soaps. Any felspar serves this purpose, so long as it is free from quartz. Labradorite from Duluth, Minnesota, is used as a sandpaper in wood-working. Other minor uses of felspar are the manufacture of tarred roofing material, for surfacing concrete, and as a poultry grit.

A great variety of processes have been devised and patented for utilising felspar as a source of potash, but these have not been able to compete with the slowly-acting geological processes which produced the Stassfurt deposits from the same material. Ground felspar used directly as a fertiliser is slow in its action, but lasting.

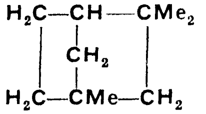
Commercial felspar is all obtained by quarrying veins of granite-pegmatite. This is a very coarse-grained rock consisting of alkali-felspar, quartz and mica, together with small amounts of tourmaline, beryl and various rare minerals. The same quarries are sometimes worked also for quartz and mica; those of California, Maine, Connecticut and Madagascar yield gem-stones; and those of southern Norway small amounts of rare-earth minerals, *e.g.* monazite, gadolinite, euxenite and uranium minerals. The felspar is, as a rule, orthoclase or microcline; but veins of soda-pegmatite, consisting mainly of albite with a little hornblende, are worked in Pennsylvania, Maryland, and at Villeneuve in Quebec. The largest producer is the United States, principally along the Appalachian Mountains in the eastern States, and in California (*v.* E. S. Bastin, Economic Geology of the Feldspar Deposits of the United States, U.S. Geol. Survey, Bull. 420, 1910; A. S. Watts, The Feldspars of the New England and North Appalachian States, U.S. Bureau of Mines, Bull. 92, 1916). In Canada the principal quarries are in Quebec and Ontario (H. S. Spence, Feldspar, Mines Branch, Ottawa, 1932, No. 731). Other large producing countries are Norway, Sweden and Italy. (On Norwegian deposits, *see* O. Andersen, T. F. W. Barth and O. A. Broch, Feltspat I–IV, Norges Geol. Undersøk. 1926–34, Nos. 128A, 128B, 141.) The spar should be free from iron-bearing minerals and mica, but the presence of 15–20% of quartz is not injurious for pottery. It is sometimes calcined before being finely ground and screened.

In the British Isles there is abundance of available material in the pegmatite-veins traversing the ancient gneisses of Sutherlandshire. The average amount of potash in the microcline of this district is 12·8%, and for the whole rock 6·7%. A few smaller pegmatite-veins are present in Cornwall; and the well-known Cornish china-stone is rich in partly altered felspar. The discovery of a vein of red felspar at Belleek in Co. Fermanagh led to the establishment of porcelain works at this locality. The red felspar becomes white on calcination, the iron passing into the condition of magnetite, the particles of which may be removed by means of a magnet. Other Irish occurrences are known in Co. Mayo and Co. Donegal. The abundantly occurring granites of Cornwall, Scotland and Ireland contain, on an average, about 5% of potash, a portion of which is, however, carried in the mica. (*v.* Special Reports on the Mineral Resources of Great Britain, Mem. Geol. Survey, vol. v. 1916, 2nd edit., 1917; P. G. H. Boswell, British Supplies of Potash-Felspar, considered from the Glass-Making point of view, J. Soc. Glass Technology, 1918, **2**, 35–71; Felspar, Imp. Mineral Resources Bureau, London, 1920.)

L. J. S.

"FEMERGIN" (*v.* Vol. IV, 330*b*).

FENCHANE.



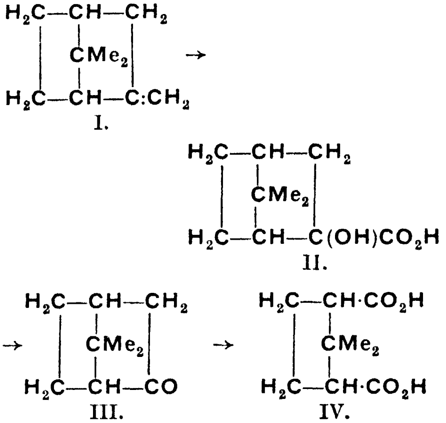
The hydrocarbon, fenchane, $C_{10}H_{18}$, b.p. 149°/750 mm., d_4^{20} 0·8316, n_D^{20} 1·4412, $[\alpha]_D$ −18°·11, has been prepared by the action of sodium ethoxide on *d*-fenchone hydrazone (Wolff and Nolte, Annalen, 1912, **394**, 97; Komppa and Hasselström, *ibid.* 1932, **496**, 164; **497**, 116), by the distillation of the hydrazone with potassium hydroxide (Kishner, J. Russ. Phys. Chem. Soc. 1911, **43**, 584) and by the reduction of α-fenchene dibromide (Qvist, Annalen, 1918, **417**, 293). It yields on nitration a mixture of 2- and 6-*nitrofenchanes* (Nametkin, J. Russ. Phys. Chem. Soc., 1915, **47**, 1590.)

J. L. S.

FENCHENES. By the removal of hydrogen chloride from fenchyl chloride, prepared by the action of phosphorus pentachloride on fenchol, Wallach (Annalen, 1891, **263**, 129; 1895, **284**, 331; 1898, **300**, 294, 319) prepared an optically inactive hydrocarbon, $C_{10}H_{16}$, b.p. 158–160°, designated fenchene. Subsequent investigations by Wallach and by many others (Wallach, *ibid.* 1908, **362**, 186; Aschan, Ber. 1907, **40**, 2750; Annalen, 1912, **387**, 1; Komppa and Hintikka, Ber. 1914, **47**, 936; Komppa and Roschier, Annalen, 1929, **470**, 129; Qvist, *ibid.* 1918, **417**, 288; Ruzicka and Liebl, Helv. Chim. Acta, 1923, **6**, 267; and Komppa and Nyman, Annalen, 1938, **535**, 252) showed that this hydrocarbon was not homogeneous but a mixture of five hydrocarbons in varying proportions. For the preparation of these hydrocarbons three general methods are available: (i) dehydration of the alcohols, fenchol and *iso*fenchol; (ii) distillation of their xanthogenates; and (iii) removal of hydrogen chloride from fenchyl and *iso*fenchyl chlorides.

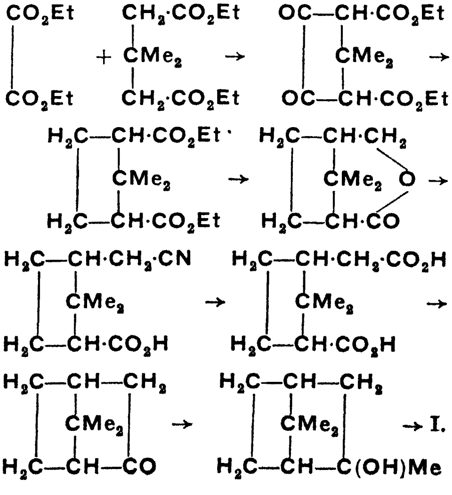
α-**Fenchene** (I) is most conveniently prepared by the distillation of methyl α-fenchyl xanthate or by the action of nitrous acid on fenchylamine. For *l*-α-fenchene prepared from *l*-fenchylamine the following constants are given: b.p. 156–157°, d^{19} 0·869, n_D^{19} 1·4724, $[\alpha]_D$ −32·12°. α-Fenchene is readily characterised by the preparation of the crystalline *dibromide*, *d*- and *l*-, m.p. 87–88°, *dl*-, m.p. 62°.

On oxidation with potassium permanganate α-fenchene (I) yields *l-hydroxy-α-fenchenic acid* (II), *d*- and *l*-, m.p. 153–154°, giving on further oxidation with lead peroxide *α-fenchocamphorone* (III), *d*- and *l*-, m.p. 109–110°, b.p. 202°, *semicarbazone*, m.p. 220–221°. On oxidation with nitric acid α-fenchocamphorone gives cis-apo*camphoric acid* (IV). α-Fenchocamphorone is obtained also by the oxidation of α-fenchene with ozone.

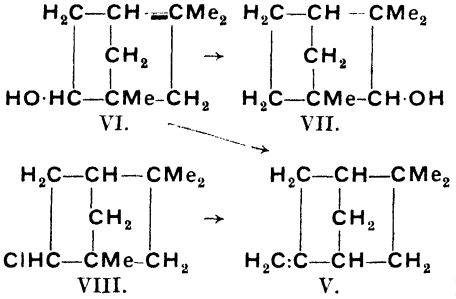


I. II. III. IV.

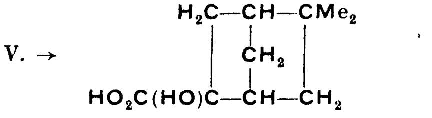
The structure assigned to α-fenchene was confirmed by Komppa's synthesis (Ber. 1901, **34**, 2472; Annalen, 1909, **368**, 126) of *apo*camphoric acid extended later to a synthesis of *dl*-α-fenchocamphorone and *dl*-α-fenchene (Ber. 1911, **44**, 1536; Komppa and Roschier, Ann. Acad. Sci. Fennicæ, 1916, [A], **10**, [iii], 3; Komppa and Komppa, Ber. 1936, **69** [B], 2606). The synthetic hydrocarbon had b.p. 154–156°, d_4^{20} 0·8660, n_D^{20} 1·47045. The main stages in these syntheses are given below.

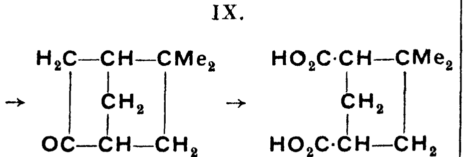


d-β-**Fenchene** (V) was first prepared by Bertram and Helle (J. pr. Chem., 1900, [ii], **61**, 353) by the dehydration of *l*-iso*fenchol* (VI), and later by Wallach and Neumann (Annalen, 1901, **315**, 381) by the action of aniline on a fenchyl chloride which had been prepared by the action of phosphorus pentachloride on *l*-α-fenchol in ligroin the reaction mixture not being cooled. It is probably best prepared either by the dehydration of *l-α-fenchol* (VII) with potassium hydrogen sulphate (Komppa and Roschier, *l.c.*; *cf.* Komppa and Nyman, *l.c.*) or by the action of toluidine on *l*-iso*fenchyl chloride* (VIII) (Qvist).


VI. VII. VIII. V.

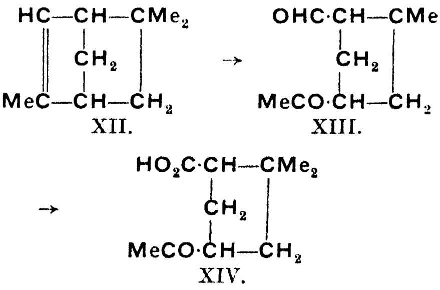
l-β-Fenchene has b.p. 150–153°, d_4^{20} 0·8591, $n_D^{18·6}$ 1·4645, $[\alpha]_D$ +62·91°. It yields a crystalline *dibromide*, m.p. 81–82° and a *nitrosochloride*, m.p. 120°. On oxidation with potassium permanganate it gives *l-hydroxy-β-fenchenic acid* (IX), *d*-, m.p. 137–138°, *dl*-, m.p. 125–126°, from which *β-fenchocamphorone* (X), m.p. 62–63°, *dl*-, m.p. 64–66° is obtained on further oxidation with lead peroxide. On oxidation with nitric acid β-fenchocamphorone gives *apofenchocamphoric acid* (XI), *cis*-, m.p. 144·5–145°, *trans*-, m.p. 147–148°.


IX.


X. XI.

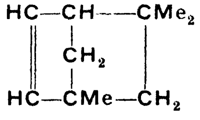
β-Fenchocamphorone is obtained also when β-fenchene is oxidised with ozone. *apo*Fenchocamphoric acid has been synthesised by Short (J.C.S. 1927, 961) and its higher homologue, homo*apo*fenchocamphoric acid, by Bardhan, Banerji and Bose (*ibid.* 1935, 1127), whilst Komppa and Komppa (Ber. 1936, **69** [B], 2606) have described a synthesis of β-fenchocamphorone although the pure ketone was not isolated. By the action of magnesium methyl iodide on β-fenchocamphorone Komppa and Roschier (Ann. Acad. Sci. Fennicæ, 1917, [A], [x], **15**, 1) prepared methyl β-fenchocamphorol which on dehydration gave a mixture of β- and γ-fenchenes.

γ-**Fenchene** (XII), b.p. 145–147°, d_4^{20} 0·8547, n_D^{20} 1·46072, which has not been obtained pure, may be prepared by the dehydration of α-fenchol with potassium hydrogen sulphate. Its structure is proved by its oxidation with ozone to the *keto-aldehyde*, $C_{10}H_{16}O_2$, (XIII), *disemicarbazone*, m.p. 219°, and to the *ketonic acid*, $C_{10}H_{16}O_3$, (XIV), *semicarbazone*, m.p. 220–221°, the latter yielding on further oxidation with sodium hypobromite *trans-apo*fenchocamphoric acid.


XII. XIII. XIV.

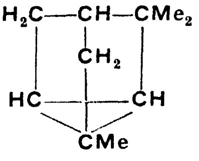
Derivatives of γ-fenchene have been prepared by Alder and Stein (Annalen, 1933, **501**, 28; 1935, **515**, 171) and by Komppa and Beckmann (*ibid.* 1933, **503**, 130). These comprise a *nitrosochloride*, m.p. 150°, a *nitrosate*, m.p. 146–147° and an *additive compound* with phenyl azide *dl*- m.p. 148–149°; *d*-, m.p. 177°.

δ-**Fenchene**



also known as *fenchylene* and iso*fenchylene* b.p. 139–140°/762 mm., d_4^{20} 0·8381, n_D^{20} 1·4494, $[\alpha]$ − 68·76° (in alcohol), has not been obtained pure. It is present in the lowest boiling fractions of the oil obtained by the dehydration of α-fenchol with potassium hydrogen sulphate or by the distillation of *l*-methyl *iso*fenchyl xanthate (Nametkin, J. pr. Chem. 1923, [ii], **106**, 26). It has been characterised by the preparation of a *nitrosochloride*, m.p. 142°, and a *nitrosite*, m.p. 163°. Its structure is proved by its oxidation to *iso*fencho-camphoric acid. It forms two *adducts* with phenyl azide, m.p. 128–129° and 122°, respectively (Alder and Stein, Annalen, 1935, **515**, 180).

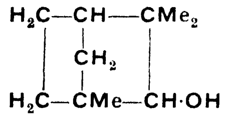
*cyclo***Fenchene**



b.p. 143–143·5°/748 mm., $d_4^{16.4}$ 0·8624, $n_D^{16·2}$ 1·45370, is present in the mixture of fenchenes prepared by any of the general methods. It is most conveniently obtained by treating *d*-fenchone hydrazone with mercuric oxide in the presence of alkali (G.P. 353933). Owing to its stability it can be readily freed from unsaturated hydrocarbons by treatment with potassium permanganate. By the action of bromine *a*-fenchene dibromide, m.p. 86–87°, is obtained, whilst on hydration *iso*fenchol is formed.

J. L. S.

FENCHOL. (*Fenchyl alcohol*)



The occurrence in nature of dl-*fenchol* was first observed in yellow pine oil distilled from the roots of *Pinus palustris* (Schimmel's Report, 1910, April, p. 107) and later confirmed by Zeitschel and Todenhöfer (*ibid.* 1932, 63, 64). The alcohol has been shown by Schmidt and Schulz (*ibid.* 1935, 94; *cf.* Komppa and Beckmann, Ber. 1935, **68** [B], 10) to be pure dl-*a*-*fenchol*, m.p. 38°, b.p. 199·5°/750 mm. d^{40} 0·9420, n_D^{40} 1·47013, *phenylurethane*, m.p. 104°, *hydrogen phthalate*, m.p. 169°. dl-*β*-*Fenchol*, m.p. 6·3°, b.p. 200·5°/750 mm., d^{40} 0·9428, n_D^{40} 1·47033, *phenylurethane*, m.p. 90·5°, *hydrogen phthalate*, m.p. 153·5°, has been prepared by Schmidt and Schulz by the hydrogenation of *dl*-fenchone using a nickel catalyst. The *d*- and *l*-fenchols have been prepared by the reduction with sodium and alcohol of the *d*- and *l*-fenchones, the *d*-ketone yielding the *l*-alcohols (Bertram and Helle, J. pr. Chem. 1900, [ii], **61**, 294). The separation of the mixture of alcohols so obtained was first carried out by Kenyon and Priston (J.C.S. 1925, **125**, 1472). Schmidt and Schulz give the following constants for the alcohols and their derivatives:

	M.p., °C.	B.p., °C./ 750 mm.	*d*	$[a]_D$ (in alcohol)	Phenyl-urethane, m.p., °C.	Hydrogen phthalate, m.p., °C.
d-*a* .	47	—	—	+11·5°	81	145·5
l-*a*- .	48	199·5	$0·9605^{20°}$	−11°	81–82	146
d-*β*- .	—	—	—	−21·50°	89	151
l-*β*- .	5·6	200·5	$0·964^{15°}$	+21·40°	89–90	152

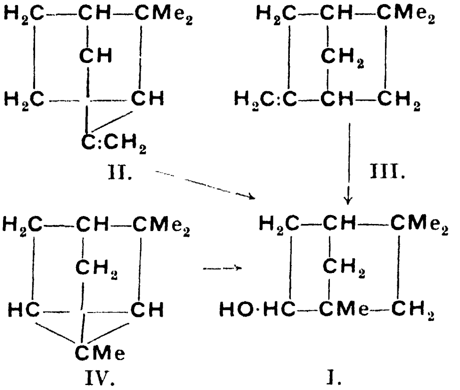
The configuration of these alcohols has not been determined (Komppa and Beckmann, Annalen, 1936, **522**, 137; Alder, Stein and Rickert, *ibid.* 1936, **525**, 225).

The fenchols are formed also by the hydration of *a*- and *β*-pinenes as was first observed by Bouchardat and Lafont (Compt. rend. 1887, **105**, 1177; 1897, **125**, 111). On oxidation they yield fenchone, whilst on dehydration a mixture of the fenchenes is obtained. Replacement of the hydroxyl group by chlorine results in the formation of a mixture, one of the constituents of which is the true fenchyl chloride (*inter al.* Komppa and Hintikka, Ber. 1913, **46**, 645; Komppa and Bergmann, Annalen, 1934, **509**, 51).

J. L. S.

*iso*FENCHOL.

l-*a*-iso*Fenchol* (*l*-*a*-iso-*Fenchyl alcohol*) (I) was prepared by Bertram and Helle (J. pr. Chem. 1900, [ii], **61**, 300; Wallach and Vivek, Annalen, 1908, **362**, 191) by the hydration of *l*-*a*-fenchene (II) with sulphuric-acetic acids. It has been prepared also by the hydration of *d*-*β*-fenchene (III) and *d*-*cyclo*fenchene (IV) (Aschan, Ber. 1907, **40**, 2750; Qvist, Annalen, 1918, **417**, 278). *d*-*a*-iso*Fenchol* has been prepared in a similar manner.



By the catalytic hydrogenation of *dl*-*iso*-fenchone Alder, Stein and Rickert (Annalen, 1936, **525**, 221) have prepared *dl*-*β*-iso*fenchol*, which is converted into the *a*-alcohol by the action of sodium in toluene solution. The latter alcohol is formed also by the reduction of *iso*fenchone with sodium and alcohol. According to Komppa and Beckmann (*ibid.* 1936, **522**, 137) the *a*-alcohol has the *exo*-configuration. The constants of the alcohols and their derivatives are given in the table (*cf.* Schmidt and Todenhöfer, Schimmel's Report, 1937, 111).

iso-Fen-chol.	M.p., °C.	B.p., °C.	d^{15}	n_D^{15}	$[a]_D$
l-*a*-	61·5–62	201–202	0·9613	1·48005	−25·73°
d-*β*-	+8	196–197	0·952	1·47259	+15·20°
dl-*a*-	42–43	202–203	0·9533	1·47556/20°	—
dl-*β*-	—	89/15 mm.	—	—	—

iso-Fen-chol.	Phenylurethane, m.p., °C.	Hydrogen phthalate, m.p., °C.
l-*a*- . . .	106–107	156
d-*β*- . . .	liquid	80
dl-*a*- . . .	94–95	—
dl-*β*- . . .	101	104–105

On oxidation the *iso*fenchols give *iso*fenchone.

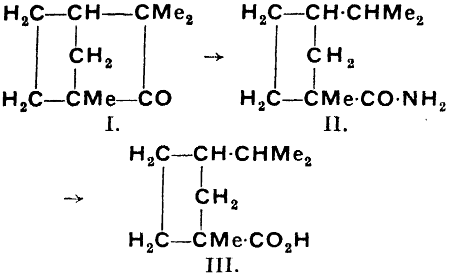
J. L. S.

FENCHONE.

The ketones *d*- and *l*-*fenchone*, $C_{10}H_{16}O$ (I), occur respectively in oil of fennel (from (*Fœniculum vulgare*) and thuja oil (from *Thuja occidentalis*) (Schimmel's Report, 1890, April, p. 20; Wallach, Annalen, 1891, **263**, 129; 1892, **272**, 102). The ketone, which has an odour reminiscent of that of camphor, has m.p. 5–6°, b.p. 192–193°, d^{18} 0·948, n_D^{18} 1·46355, $[a]_D$+62·76°, *oxime*, *d*- and *l*-, m.p. 164–165°, *dl*-, m.p. 158–160°, *semicarbazone*, *d*- and *l*-, m.p. 182–183°, *dl*-, m.p. 172–173°.

The structure (I), now assigned to the ketone, was first suggested by Semmler (Chem.-Ztg.

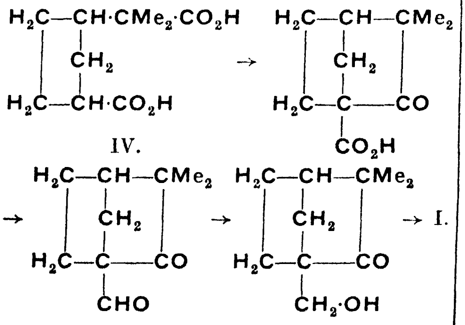
1905, **29**, 1939) who showed (Ber. 1906, **39**, 2578) that, when it was heated with sodamide, ring fission occurred with the formation of *d-fencholamide* (II) giving on hydrolysis with alkali *d-fencholic acid* (III), which Wallach (Annalen, 1909, **369**, 73) later showed was formed also when the ketone was fused with alkali.



I. II. III.

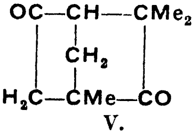
The investigations of Bouveault and Levallois (Compt. rend. 1908, **146**, 181; Bull. Soc. chim. 1910, [iv], **7**, 542, 683, 736, 807, 963, 968) established the structure of fencholic acid, which they ultimately synthesised.

Rigid proof of the structure of fenchone has been furnished by the synthesis of the *dl*-ketone from methylnorcamphor (Ruzicka, Ber. 1917, **50**, 1362) and from *dl-cis*-camphenecamphoric acid (IV) (Komppa and Klami, *ibid.* 1935, **68** [B], 2001), the more important stages in the latter synthesis being given below:



IV.

On reduction fenchone gives fenchol (*q.v.*). The ketone is very resistent to the action of most oxidising agents. On oxidation with chromic acid it gives the *diketone* (V) (Bredt, J. pr. Chem. 1923, [ii], **106**, 338) and with concentrated nitric acid, *iso*camphoronic, *aa*-dimethyltricarballylic, dimethylmalonic and *iso*butyric acids (Gardner and Cockburn, J.C.S. 1898, **73**, 708).



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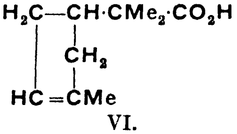
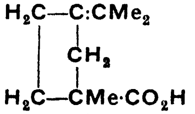


VI.



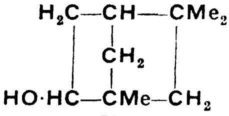
VII.

Like camphor oxime, fenchone oxime cannot be reconverted into the ketone by hydrolysis. When digested with dilute sulphuric acid it gives two unsaturated nitriles, α- and *β-fencholenonitriles* (Wallach, Annalen, 1890, **259**, 329; 1892, **269**, 332; 1901, **315**, 278; 1911, **379**, 182; Cockburn, J.C.S. 1899, **75**, 501). The former of these is the nitrile of *α-fencholenic acid*, b.p. 136–138°/12 mm., probably represented by (VI) and the latter of *β-fencholenic acid*, m.p. 72–73° (VII), which has been prepared synthetically (Ruzicka, Ber. 1917, **50**, 1362).

Reduction of fenchone oxime with sodium and alcohol gives a mixture of *fenchylamines*, obtained also by heating fenchone with ammonium formate (Wallach, Annalen, 1891, **263**, 140; 1892, **269**, 358; 1893, **272**, 105; **276**, 318). The catalytic hydrogenation of *d*-fenchone oxime gives a *d-fenchylamine*, *hydrochloride*, m.p. 293°, *picrate*, m.p. 199° (Alder, Stein and Rickert, *ibid.* 1936, **525**, 221). *l*-Fenchylamine reacts in an abnormal manner with nitrous acid, giving a mixture of cineole, *d*-limonene, dipentene and *l*-α-fenchene (Wallach, *ibid.* 1908, **362**, 117).

J. L. S.

isoFENCHONE. *l*-iso*Fenchone*, $C_{10}H_{16}O$ (I), b.p. 201°, $d^{18\cdot5}$ 0·943, $n_D^{18\cdot5}$ 1·4621, a_D −9·35°, was prepared by Bertram and Helle (J. pr. Chem. 1900, [ii], **61**, 303) by the oxidation of *l*-α-iso*fenchol* (II) with chromic acid, Wallach (Annalen, 1907, **357**, 56; 1908, **363**, 4) later preparing the *d*-ketone from *d*-α-*iso*fenchol. The *d*- and *l*-*oximes* have m.p. 82°, *d*- and *l*-*semicarbazones*, m.p. 221–222°, *dl*-, m.p. 223–224°.



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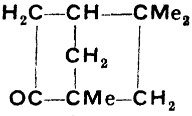
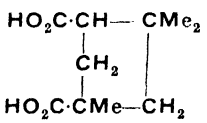
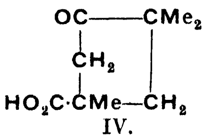


I.

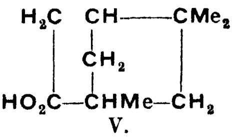


III.

Oxidation of *iso*fenchone with potassium permanganate gives iso*fenchocamphoric acid* (III) (Wallach, *ibid.* 1908, **362**, 196; **363**, 5) the reactions of this acid having been studied in detail by Aschan (*ibid.* 1912, **387**, 1; *cf.* Sandelin, *ibid.* 1913, **396**, 285). iso*Fenchononic acid* (IV), prepared by Aschan by the degradation of *iso*fenchocamphoric acid has been synthesised by Bardhan and Ganguly (J.C.S. 1936, 1852). On fusion with potassium hydroxide *iso*fenchone yields iso*fencholic acid* (V). On reduction with sodium and alcohol the ketone yields *β-iso*fenchol (Schmidt and Todenhöfer, Schimmel's Report, 1937, 112).



IV.



V.

J. L. S.

FENCHYLENE, δ-fenchene (*v.* Fenchenes).

FENNEL. The dried ripe fruit (seed) of *Fœniculum vulgare* Miller (Fam. Umbelliferæ), cultivated extensively on the Continent of Europe and in North America. It is a biennial or perennial aromatic herb, with leaves divided into numerous hair-like segments, and grows to a height of 3–5 ft. The cremocarp consists of, and is more or less separated into, two straight or but slightly curved mericarps, from 5 to 10 mm. long and 1·5–4 mm. broad. The cross-section of the mericarp is almost that of an equal-sided pentagon, the commisural surface being greater than the four comprising the dorsal surface. It also exposes six vittæ, one on each dorsal and two on the commisural side with five almost equally prominent ridges. It is largely used as an aromatic and carminative, particularly as a corrigent of senna and rhubarb. It is stated that the oil is usually prepared from the whole herb.

Microscopic Appearance.—The outer epidermis is composed of quadrangular to polygonal cells with an unstriated cuticle (distinction from many other umbelliferous fruits) with occasional stomata. The mesocarp consists of very characteristic, lignified reticulate parenchyma, and the inner epidermis of thin-walled cells almost reminiscent of parquet. The endosperm is composed of colourless, rather thick-walled parenchyma, which contain aleurone grains and rosette crystals of calcium oxalate.

Chemical Composition.—Probably the most satisfactory method of determining the essential oil content of fennel is by the process of Cocking and Middleton (Quart. J. Pharm. 1935, **8**, 435). The powdered fruit is mixed with brine and distilled, the vapours being passed through the top of a condenser into a graduated tube, in which the oil is collected, whilst the condensed water is returned to the distillation flask. An air inlet and outlet is provided below the condenser, but above the graduated tube. These authors find that the yield of oil is increased by crushing the fruit before distillation, but that the commercial powder looses some of its oil on keeping. The fruits contain from 3 to 4% of oil in the freshly ground fruit and from 1 to 2% less in the commercial powder.

Standards.—The British Pharmacopœia requires fennel to contain not more than 2% of foreign organic matter nor more than 12% of ash.

Adulteration.—French sweet fennel, *Fœniculum vulgare,* subsp. *capillaceum,* var. *dulce,* is sometimes substituted for bitter fennel. It contains only about 2% of volatile oil, which is practially free from fenchone. Japanese and Indian fennels are sometimes substituted, as is also, occasionally, extracted fruit, which last are much darker in colour than the unextracted fruit.

T. McL.

FENNEL, ESSENTIAL OIL OF. The oil distilled from the fruits of *Fœniculum vulgare* Mill. or *F. capillaceum* Gilib. (Fam. Umbelliferæ). The herb is cultivated in Galicia, Germany, Russia, Roumania, Egypt, Asia Minor, Persia, India and Japan. Inferior oils are obtained from the wild bitter fennel and the water fennel (*Œnanthe phellandrium, Phellandrium aquaticum*).

Constituents.—Fennel oil contains anethole, fenchone, pinene and dipentene. The proportion of anethole varies considerably and is roughly indicated by the congealing point which serves to determine the quality of the oil. The proportion of fenchone also varies from almost nil to 22%, but this constituent is of little importance.

Characters.—Sp.gr. 0·960–0·995, opt. rotation +6° to +20°. Congealing point +5° to +10°. Solubility 1 in 5 to 8 vol. of 80% alcohol. The congealing point is determined by the method described in the British Pharmacopœia for aniseed oil, but a small crystal of anethole must be used to induce crystallisation after cooling.

C. T. B.

"*FERAN*" *v.* Aluminium (Vol. I, 278*d*).

FERBERITE, the name applied to the members at the iron end of the wolframite series ($FeWO_4$).

FERGANITE is related to carnotite (*v.* Vol. II, 393*a*).

L. J. S.

FERGUSONITE. A rare mineral consisting of columbate (niobate) and tantalate of yttrium and cerium earths together with a small amount of uranium, the general formula being

$$R'''(Cb,Ta)O_4.$$

Tetragonal crystals were found in Greenland in 1826, but usually the mineral is massive with a lustrous, pitchy appearance on the fractured surfaces; sp.gr. 5·8. It is optically isotropic, owing to alteration and hydration: when heated, it suddenly shows an incandescent glow, becomes fractured and anisotropic, and gives off gases (helium, etc.). The mineral occurs in pegmatite-veins at Ytterby in Sweden, near Arendal and elsewhere in Norway, and in some abundance as large masses at Barringer Hill in Llano Co., Texas. At the last-named locality it has been mined, together with gadolinite and other rare-earth minerals, for the supply of yttrium, etc. Other localities are Coolegong in Western Australia, Madagascar, and the Caucasus.

L. J. S.

FERMENLACTYL, a preparation of lactic acid bacilli.

FERMENTATION, ALCOHOLIC. The production of carbon dioxide and alcohol from sugar is by far the most important of all technical processes of fermentation, and has, therefore, been more thoroughly investigated than any other change produced by micro-organisms. Although both alcohol and carbon dioxide are produced from sugar by many micro-organisms belonging to the class of bacteria, the power of bringing about the typical alcoholic fermentation, of decomposing sugar almost quantitatively into these two substances, is possessed among micro-organisms only by certain moulds and by a group of unicellular fungi which belong to several closely allied families and are commonly grouped together as yeasts. The biology and mode of culture of these are treated in the article on BREWING.

Species of bacteria are known which decompose as much as 90% of the fermented sugar into alcohol and carbon dioxide. Thus *Thermobacterium mobile* Lindner, gives a yield of alcohol and carbon dioxide of this order and moreover displays many of the other chemical characteristics of yeast (decomposition of pyruvic acid, phosphorylation of glucose, etc.) (*see* Kluyver, Ergebn. Enzymforsch. 1935, **4**, pp. 237–8). The remaining 10% of the sugar is converted into lactic acid. A similar large yield of alcohol and carbon dioxide is given by *Zymosarcina ventriculi* Smit, but in this case small quantities of hydrogen and formic and acetic acids are also produced.

COMPOSITION OF YEAST.—The cell consists of membrane, cytoplasm and nucleus, but much doubt exists as to the exact form of the nucleus and the changes which it undergoes during fermentation, budding and spore formation. In the cytoplasm occur vacuoles, and at various stages in the life of the cell granules of chromatin and volutin are formed as well as fat droplets and glycogen.

Yeast, which has been pressed at about a half-ton per square inch, forms a friable, almost white mass, containing about 70% of water and alcohol, and 30% of solids. The composition of the dry matter of yeast varies so greatly with conditions of growth, etc., that no general statement is of much value. The ash, which amounts to 5–10% of the dry residue, consists essentially of potash (K_2O, 28–39%), magnesia (MgO, 4–6%), lime (CaO, 1–7%), and phosphoric oxide (P_2O_5, 45–59%), together with smaller quantities of sulphur trioxide, iron, silica, and traces of chlorine. The exact nature of the cell membrane is as yet undecided, largely because no satisfactory method of removing the cell contents without alteration of the membrane has been devised (*see* Zechmeister and Tóth, Biochem. Z. 1934, **270**, 309; 1936, **284**, 133; Sevag, Cattaneo, and Maiweg, Annalen, 1935, **519**, 111). It appears to contain a polysaccharide of the composition of a hexosan, but differing in its properties from cellulose. It may possibly be structurally associated with the magnesium and phosphate of the cell (McAnally and Smedley Maclean, Biochem. J. 1937, **31**, 72). Indeed Daoud and Ling (J.S.C.I. 1931, **50**, 365T, 379T) consider that it consists of the silicic and phosphoric esters of glycogen and yeast gum (itself a complex polysaccharide derived from mannose and glucose). The cytoplasm contains a coagulable albumin, a nuclein, glycogen, yeast gum and a large number of other compounds, among which may be mentioned glutathione, the B-vitamins, spermine and co-zymase.

General Phenomena of Alcoholic Fermentation.

1. THE FERMENTABLE SUBSTANCES.—All yeasts which ferment glucose also ferment mannose and fructose. The case of galactose is different, as some yeasts appear to ferment it imperfectly, and others not at all. It has been found by many observers and may now be regarded as established, that certain yeasts which do not normally ferment galactose readily acquire this property when they are cultivated in the presence of this sugar, as for example in hydrolysed lactose. Examples of this are *S. carlsberg* 1 H., *S. cerevisiœ* H., *S. thermantitonum* Johnson, etc. Indeed, according to Lindner, all the culture yeasts exhibit this property (*see* Slator, J.C.S. 1908, **93**, 217; Lindner, Woch. Brau. 1911, **28**, 61).

The conditions necessary for the acquisition of the property of fermenting galactose have been much discussed, but the experiments of Stephenson and Yudkin (Biochem. J. 1936, **30**, 506, where the literature is cited) show definitely that this can occur without increase in the number either of total or viable cells of the yeast taking place and that the acquired power is lost when the adapted yeast ferments glucose.

The higher saccharides are not directly fermentable by yeast, but must first undergo hydrolysis to the simple hexoses. This is effected by hydrolytic enzymes present in the yeast, which can, as a rule, be extracted from the cell by appropriate methods.

Willstätter and his colleagues are of the opinion that in some circumstances yeasts can ferment disaccharides (sucrose, maltose, lactose) directly. Thus cases have been observed in which (*a*) fermentation proceeds at a p_H at which the hydrolytic enzyme ceases to act; (*b*) fermentation is much more rapid than can be accounted for by the amount of hydrolytic enzyme which can be demonstrated to be present in the cell (*see* Willstätter and Steibelt, Z. physiol. Chem. 1921, **115**, 211; Willstätter and Oppenheimer, *ibid.* 1922, **118**, 168; Willstätter and Bamann, *ibid.* 1926, **151**, 242; **152**, 202; and *cf.* von Euler and Svanberg, *ibid.* 1919, **105**, 187; von Euler and Sandberg, Fermentforsch. 1925, **8**, 232; von Euler and Josephson, Z. physiol. Chem. 1922, **120**, 42). It must be remembered that some doubt exists as to the p_H of the cell contents and that in many of these cases a long induction period occurred, and the possibility of increase by adaptation in the amount of hydrolytic enzyme present must be considered.

The ordinary culture yeasts employed in brewing, etc., contain maltase and invertase, but not lactase, and are therefore able to ferment maltose and cane sugar, but not lactose. Bottom yeasts appear invariably to contain melibiase, which decomposes melibiose into glucose and galactose, whilst this enzyme is lacking in top yeast. An analytical method for detecting bottom yeast in top yeast has been founded on this fact. In addition to this, practically all culture yeasts are able partly to ferment raffinose, which on hydrolysis yields melibiose and fructose, and they probably contain a special enzyme, *raffinase*, which produces this hydrolysis, although it is possible that this is due to the invertase. In the case of top yeasts, only the fructose thus produced undergoes alcoholic fermentation, the melibiose remaining unaltered, whereas the bottom yeasts decompose this also. Dextrin is also more or less slowly fermented by yeast, the hydrolysis being effected by a dextrinase or amylase. This property is of great importance in brewing, as a yeast which possesses a comparatively large amount of this enzyme is able to attenuate the wort to a greater extent, and to produce a larger yield of alcohol. Starch and glycogen are unaffected by yeast, probably because, owing to their highly colloidal nature, they are unable to penetrate the cell. Species of yeast are now known which are lacking in one or other of all these hydrolytic enzymes and are incapable of fermenting the corresponding sugar. These yeasts have frequently been employed for the isolation of such a sugar as maltose from mixtures containing glucose or fructose, and for the analytical estimation of mixtures of sugars (Davis and Daish, J. Agric. Sci. 1913, **5**, 437), and of the sugars in urine (*see* Harding and Grant, J. Biol. Chem. 1931, **94**, 529; Harding, Nicholson and Grant, *ibid.* 1932–33, **99**, 625). Their relations to the disaccharides are employed as a means of classification. Thus *S. marxianus* H. and *S. exiguus* H. ferment cane sugar, but not maltose; *S. rouxii* Boutroux ferments maltose, but not cane sugar; *S. fragilis* Jörg. found in kefir, ferments lactose, and *S. mali* Duclaux only ferments the simple sugars and is without action on the disaccharides. No yeast appears to be able to ferment the synthetic disaccharides, such as *iso*maltose or glucosidogalactose, and this disability extends to the isomerides of the hexoses, such as sorbose, tagatose, etc., to the optical antipodes of the fermentable sugars which have been obtained by synthesis, and to the pentoses and tetroses. Beyond the simple sugars mentioned above, no other substance appears to be directly fermentable by yeast to alcohol and carbon dioxide, with the exceptions of a synthetic 9-carbon-atom sugar and of glyceraldehyde and dihydroxyacetone, which, according to Bertrand (Ann. Chim. Phys. 1904, [viii], **3**, 181), Buchner and Meisenheimer (Ber. 1910, **43**, 1773) and von Lebedev (*ibid.* 1911, **44**, 2932; 1912, **45**, 3526; Biochem. Z. 1912, **46**, 483), are acted on by yeast. Glycerol, and the higher alcohols such as mannitol and dulcitol, are not fermented.

The phosphorylated intermediate products of alcoholic fermentation are decomposed by yeast preparations, but not all of them are attacked by living yeast, possibly owing to the limited permeability of the yeast cell membrane. Thus hexosediphosphate is unattacked by living yeast whereas fructose-6-phosphate is slowly fermented (Neuberg, Biochem. Z. 1918, **88**, 432), as is also *d*-phosphoglyceraldehyde (Smythe and Gerischer, *ibid.* 1933, **260**, 414).

In 1911, Neuberg (*ibid.* 1911, **31**, 170) made the important discovery that yeast decomposes α-ketonic acids quantitatively into carbon dioxide and the corresponding aldehyde (*see* p. 23).

$$R{\cdot}CO{\cdot}COOH = R{\cdot}CHO + CO_2$$

This reaction is brought about by all races of brewer's yeast, and by wine yeasts, and has been traced to the presence in these of an enzyme termed by Neuberg *carboxylase.* The enzyme passes from the cell into the yeast juice, so that this also possesses the property of decomposing α-ketonic acids. Their salts are also attacked, the carbonate or bicarbonate of the metal being formed, and a certain amount of the aldehyde undergoing condensation to inactive aldol under the influence of the alkaline carbonate. The enzyme is undoubtedly distinct from zymase, and is differently affected by agents such as heat and antiseptics. Its action is, moreover, independent of the presence of the co-zymase of yeast juice (Harden, Biochem. J. 1913, **7**, 214; Neuberg and Rosenthal, Biochem. Z. 1913, **51**, 125) but requires a specific co-enzyme (Auhagen, Z. physiol. Chem. 1931, **204**, 149) (*see* p. 18).

Many hydroxy-acids are also slowly attacked by yeast, among these being lactic acid (Buchner and Meisenheimer, Ber. 1904, **37**, 417; 1905, **38**, 620; 1906, **39**, 3201; Oppenheimer, Z. physiol. Chem. 1914, **89**, 45), glyceric acid (Neuberg and Tir, Biochem. Z. 1911, **32**, 323; von Lebedev, Ber. 1914, **47**, 660), gluconic acid, and glyoxylic acid (von Lebedev, Biochem. J. 1918, **12**, 81).

2. The Rate of Fermentation by Yeast has been investigated by many authors. It is best examined by Slator's method of adding a suspension of yeast to the solution to be fermented, and determining the initial rate of fermentation. In this way, all errors due to change in the amount and condition of the yeast and to the influence of the products of decomposition are, to a large extent, avoided (J.C.S. 1906, **89**, 128). By this and other methods, it has been established (*see* Hopkins and Roberts, Biochem. J. 1935, **29**, 919, where the literature is cited) that the kinetics of fermentation by living yeast are precisely similar to those of an enzyme reaction. With low concentrations of sugar and relatively high concentrations of yeast (0·04–0·07% glucose and 5·4 g. pressed yeast per 100 c.c. at 30°) a unimolecular reaction occurs. When relatively low concentrations of yeast are used (as in Slator's experiments), the enzyme becomes saturated and the fermentation rate remains constant over a long range of substrate concentration. Intermediate conditions, as in the experiments of Nord and Weichherz (Z. Elektrochem. 1929, **35**, 612), result in a maximum rate followed by a decline.

The rate increases with the temperature, but the temperature coefficient diminishes as the temperature increases. The following values were obtained by Slator for glucose; they are independent of the concentration of yeast and glucose, the class of yeast and presence or absence of nutrient materials, and remained the same when inhibiting agents are present:

Temp.	V_{t+10}/V_t
5°	5·6
10°	3·8
15°	2·8
20°	2·25
25°	1·95
30°	1·6

The temperature coefficient for an ordinary chemical reaction is of the same order as these numbers, viz. 2–3 for 10°. Slightly higher coefficients were obtained by Hopkins and Roberts (Biochem. J. 1935, **29**, 2486).

At moderate concentrations glucose and fructose are fermented at the same rate, and this is also the case when the fermenting power of the yeast is partly destroyed by heat, antiseptics, etc. On the other hand, mannose and galactose may be fermented at a rate different from that of glucose, and the rates are differently affected by inhibiting agents. The temperature coefficients for fructose and mannose are the same as for glucose, that for galactose is slightly less.

Whilst, as just stated, fructose is fermented by most yeasts at approximately the same rate as glucose at concentrations of about 2–8%, at low concentrations fructose is fermented much more slowly than glucose (Hopkins and Roberts, Biochem. J. 1935, **29**, 931), and it has been calculated that the dissociation constant (K_m) of the compound of enzyme and sugar is 0·0106 for glucose and 0·0225 for fructose. This has an important bearing on the remarkable fact that many yeasts which ferment glucose and fructose at approximately the same rate, nevertheless remove glucose more rapidly than fructose from a mixture of equal parts of the two (*see* Sobotka and Reiner, *ibid.* 1930, **24**, 926, where the literature is cited and discussed). On the other hand yeasts have been described, especially Sauterne yeasts (*see* Sobotka and Reiner, *ibid.* 1930, **24**, 1783) which ferment fructose 50–100% more rapidly than glucose at all concentrations and also remove fructose more rapidly than glucose (or mannose) from mixtures of equal parts of the two. This property is expressed by a selectivity factor. Thus for glucose and fructose

$$K_{g/f}=\frac{ln y_0 - ln y}{ln z_0 - ln z}$$

where y_0 and z_0 are the initial concentrations of the sugars and y, z the concentrations at any given time. This factor according to Hopkins and Roberts is closely related to the ratio of the dissociation constants of the compounds of the enzyme with the sugars in question.

Hopkins and Roberts consider that the actual substance fermented is, in the case of glucose, a form of the sugar intermediate between the α- and β-forms (*ibid.* 1936, **30**, 76), and in the case of fructose one component of the αβ-equilibrium mixture, the limiting rate being that at which this form can be restored by mutarotation of the other form (*ibid.* 1935, **29**, 2486).

The Factor Z.—Extracts which greatly increase (two or three times) the rate of fermentation of sugars by living yeast (but have no effect on that of dried yeast) have been obtained by von Euler and his colleagues (*see* von Euler and Larsson, Z. physiol. Chem. 1934, **223**, 189, where the earlier literature is cited) from yeast itself and from many plants and animal organs. The active substance (Factor Z) is thermostable and relatively resistant to oxidation. It is probably identical with the *Bios* II of Lucas (J. Physical Chem. 1924, **28**, 1180; *v.* Vol. I, 692*b*).

3. Heat of Fermentation.—During the fermentation of sugar by yeast, a considerable amount of heat is evolved, so that the temperature of the mass rises as the fermentation proceeds. The quantity of heat evolved may be calculated from the difference between the heat of combustion of glucose (673·7 kg.-cal.) and that of the alcohol formed from it (2 × 325·7 = 651·4 kg.-cal.), the remaining product, the carbon dioxide, being completely oxidised. This difference amounts to 22·3 kg.-cal., so that the fermentation of 180 g. of glucose liberates enough heat to raise the temperature of 22 litres of water 1°. This theoretical number has been confirmed by the experiments of Bouffard (Compt. rend. 1895, **121**, 357), who obtained the value 23·5 kg.-cal. In the fermentation of a disaccharide, heat is also evolved by the hydrolysis to the simple sugars; but this is so small in amount, 4·5 kg.-cal. for cane sugar and 3·8 kg.-cal. for maltose (Herzog, Z. physiol. Chem. 1903, **37**, 383), that the numbers actually observed for these sugars per gram-molecule are approximately twice that for glucose (Rubner, Arch. Hyg. Bakt. 1904, **48**, 260; **49**, 355; A. J. Brown, J. Inst. Brew. 1901, **7**, 93).

4. Products of Fermentation.—The earlier observers (Lavoisier, Gay-Lussac) considered that in the process of fermentation the sugar was completely decomposed into carbon dioxide and alcohol, according to the equation:

$$C_6H_{12}O_6=2CO_2+2C_2H_6O$$

Schmidt, in 1847, however, observed the occurrence of succinic acid in all fermented liquors, and the amount of this substance formed was carefully estimated by Pasteur who also made the important observation that glycerol was an invariable product of the fermentation of sugar (Compt. rend. 1858, **46**, 857). According to Pasteur (Ann. Chim. Phys. 1860, [iii], **58**, 323), the products from 100 parts of cane sugar, which yield 105·36 parts of invert sugar, are:

Alcohol	51·00
Carbon dioxide	49·11
Succinic acid.	0·65
Glycerol	3·40
Cellulose, fat, and extractive matter	1·30
	105·46

The proportions of these products were subsequently found to be variable and to depend on the condition of the yeast, the nature of the nutrient material, etc. Many other subsidiary products have now been recognised in addition to succinic acid and glycerol. Among these may be mentioned *iso*butyleneglycol (in wine and cherry brandy), formic acid, acetic acid, propionic acid, butyric acid, and several still higher acids, (hexoic, octoic, pelargonic, decylic, œnanthylic), which occur as esters, and formaldehyde, acetaldehyde, and traces of higher aldehydes, propyl alcohol, *n*-butyl alchol, *iso*butyl alcohol, *see* butyl alcohol, *n*-amyl alcohol, *iso*amyl alcohol, and alcohols containing 6, 7 and 9 carbon atoms.

The alcohols and aldehydes mentioned above are found in the spirit obtained by the distillation of the fermented liquids. All such spirit yields a fraction of high boiling-point, which amounts to 0·1–0·7% of the whole, and is known as fusel oil (*q.v.*). The discussion which had long raged over the origin of this fusel oil was set at rest by the researches of Ehrlich (Z. Ver. Rübenzuck.-Ind. 1905, 539; Biochem. Z. 1906, **2**, 52; 1909, **18**, 391; Ber. 1906, **39**, 4072; and many other papers), who has proved in the most conclusive manner that the higher alcohols and the corresponding acids and aldehydes which are observed in fermented liquids are formed by the yeast, not from the sugar, but from the amino-acids produced by the hydrolysis of the proteins of the medium and of the yeast cell itself.

The reaction is a general one, and requires the presence of living yeast and sugar as well as the amino-acid. In these circumstances, the yeast not only ferments the sugar to alcohol and carbon dioxide in the usual way, but also brings about what Ehrlich terms the alcoholic fermentation of the amino-acids, according to the equation:

$$R\cdot CH(NH_2)COOH+H_2O = R\cdot CH_2\cdot OH+NH_3+CO_2$$

The ammonia appears to be invariably assimilated by the yeast and is not found in the medium. This fact probably affords the key to the biological significance of the reaction. It is by means of this change that the yeast acquires from the amino-acids, which are usually the chief available source of this element, the nitrogen necessary for its existence. The whole change is rendered possible by the utilisation of some of the energy evolved by the fermentation of sugar, which is proceeding simultaneously. Ehrlich has shown, by careful experiments, that in this way leucine

$$(CH_3)_2CH\cdot CH_2\cdot CH(NH_2)COOH$$

yields *iso*amyl alcohol

$$(CH_3)_2CH\cdot CH_2\cdot CH_2\cdot OH,$$

and *iso*leucine

$$C_2H_5\cdot CH(CH_3)CH(NH_2)COOH$$

yields *d*-amyl alcohol $C_2H_5\cdot CH(CH_3)CH_2\cdot OH$, which are the main constituents of fusel oil.

The other amino-acids yield corresponding products, tyrosine

$$OH\cdot C_6H_4\cdot CH_2\cdot CH(NH_2)COOH$$

being converted into *p*-hydroxyphenylethyl alcohol or tyrosol $HO\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot OH$, a substance of intensely bitter taste, and phenylalanine $C_6H_5\cdot CH_2\cdot CH(NH_2)COOH$ into phenylethyl alcohol $C_6H_5\cdot CH_2\cdot CH_2\cdot OH$, one of the chief constituents of oil of roses. Valine yields *iso*butyl alcohol, and arginine a mixture of 1:4-butyleneglycol and succinic acid (Thorne). These changes take place under practical brewing conditions (Thorne, J. Inst. Brew. 1937, **43**, 288), and it is almost certain that many of the substances which impart flavour, bouquet and aroma to fermented liquors have their origin in this manner, so that the subject is one of fundamental importance for the technologist.

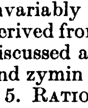
Succinic acid is also formed by a reaction of this kind, which differs from the foregoing in so far as it involves an oxidation. The source of this substance is glutamic acid which, instead of yielding γ-hydroxybutyric acid, as might have been expected, is converted into succinic acid

$$COOH\cdot CH_2\cdot CH_2\cdot CH(NH_2)COOH+2O = COOH\cdot CH_2\cdot CH_2\cdot COOH+CO_2+NH_3$$

Yeast is, moreover, not only capable of producing these changes in amino-acids naturally present in the medium or purposely added to it, but also decomposes in a similar manner the amino-acids formed by the hydrolysis of its own protein. Some of the cells evidently utilise the products of the autolysis of others which have died, and hence it comes about that even when a pure sugar solution is fermented by pure washed yeast, the fermented liquid contains a certain small proportion of fusel oil, succinic acid, etc. The amounts produced in these circumstances are, however, small, as they are also when the yeast is grown in presence of ammonium salts. Many of the products (*e.g.* tyrosol) have a strongly inhibitory effect on yeast growth and a smaller effect on fermentation (Thorne, *ibid.* 1939, **45**, 13).

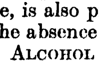
During the fermentation of sugar yeast excretes nitrogenous substances the greater part of which is not in the form of amino-acids (Lampitt, Biochem. J. 1919, **13**, 459; Thorne, J. Inst. Brew. 1933, **39**, 608; Ivanov and Krupkina, Biochem Z. 1929, **212**, 255).

It seems probable, from the experiments of Neubauer and Fromherz (Z. physiol. Chem. 1911, **70**, 326), that the amino-acid (I) first undergoes indirect oxidation to the corresponding ketonic acid (III) and ammonia, and that this acid is then decomposed by the yeast, forming carbon dioxide and an aldehyde (IV), which then either undergoes reduction to an alcohol (*e.g.* fusel oil) or oxidation to an acid (*e.g.* succinic acid).



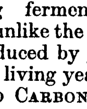
$$\begin{array}{c}R\\ \cdot\\ C\begin{smallmatrix}H\\ NH_2\end{smallmatrix}\\ \cdot\\ COOH\end{array}$$

I.



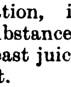
$$\begin{array}{c}R\\ \cdot\\ C\begin{smallmatrix}OH\\ NH_2\end{smallmatrix}\\ \cdot\\ COOH\end{array}$$

II.



$$\begin{array}{c}R\\ \cdot\\ CO\\ \cdot\\ COOH\end{array}$$

III.



$$\begin{array}{c}R\\ \cdot\\ CHO\end{array}$$

IV.

It is interesting to note that the reaction proceeds asymmetrically.

It has now been proved by Neuberg and his colleagues (*v. post*) that the glycerol, which is invariably formed during fermentation, is derived from the sugar and, unlike the substances discussed above, is also produced by yeast juice and zymin in the absence of living yeast.

5. Ratio of Alcohol to Carbon Dioxide. All these decompositions have an influence on the ratio of alcohol to carbon dioxide produced by alcoholic fermentation. The theoretical ratio is 46/44=1·045, and Pasteur, as quoted above, actually found 51·00 parts of alcohol to 49·11 of carbon dioxide from 100 of cane sugar. He, however, considered that succinic acid and glycerol were formed according to the equation:

$$49C_6H_{12}O_6+30H_2O = 12C_4H_6O_4+72C_3H_8O_3+30CO_2$$

and therefore ascribed 0·61 of carbon dioxide to the fermentation which had produced 0·65 of succinic acid, thus leaving 48·50 of carbon dioxide as the product of the true alcoholic fermentation, the corrected ratio being thus 51·00/48·50=1·051. Similar results were obtained by Jodlbauer (Z. Ver. Rübenzuck.-Ind. 1888, 308), who found that cane sugar yielded 49·04% of carbon dioxide.

Buchner and Meisenheimer (Ber. 1910, **43**, 1773), working with pure yeast (Race 792 of the Berlin Collection), obtained 49·73% of the cane sugar as alcohol, and 49·12% as carbon dioxide; the ratio being 1·01. They ascribe this excess of carbon dioxide to the oxidation corresponding to the production of glycerol, the amount of which was not estimated. In spite of the fact that no nitrogenous material was added to the medium, the carbon dioxide and alcohol only represent 98·85 parts of the 105·36 of invert sugar to be accounted for, so that 6·51 parts had undergone some other change. Any carbon dioxide formed from amino-acids produced by autolysis would be included in the amount found.

6. FORMATION OF GLYCOGEN: AUTOFERMENTATION OF YEAST. Yeast very readily converts a portion of the carbohydrate present in the medium into glycogen $(C_6H_{10}O_5)_n$ which is stored in the cell (*see* Harden and Young, J.C.S. 1902, **81**, 1224, where the literature is cited).

This material acts as a reserve carbohydrate, and, when the yeast is preserved in absence of sugar solution, is slowly fermented into alcohol and carbon dioxide: this phenomenon is known as the autofermentation of yeast. As yeast may contain as much as 30–40% of its dry weight of glycogen, it follows that a very considerable amount of carbon dioxide and alcohol may be produced from yeast alone. The autofermentation proceeds more rapidly at high temperatures (Harden and Rowland, J.C.S. 1901, **79**, 1227), and is greatly accelerated by the addition of many salts (Harden and Paine, Chem. Soc. Proc. 1911, 103) and of toluene. The conditions of formation of glycogen have been investigated quantitatively by Pavy and Bywaters (J. Physiol. 1907, **36**, 149), and microscopically by Wager and Peniston (Ann. Bot. 1910, **24**, 45; Wager, J. Inst. Brew. 1911, **17**, 2).

THE ALCOHOLIC ENZYME OF YEAST.

Up to 1897 all attempts to isolate from a yeast an enzyme capable of producing alcoholic fermentation had failed. It had early been shown, at first by Mitscherlich (1841) and then by Helmholtz, that the process of fermentation in all probability took place within the cell, and the efforts of later investigators had been rightly directed towards the extraction of an enzyme by some process of disintegration or treatment with solvents. All such efforts were, however, made in vain, as were also attempts to extract the enzyme by freezing or plasmolysis, the products obtained being either inactive or owing what activity they possessed to the presence of unbroken yeast cells or bacteria (F. von Lüdersdorff, Schmidt, Pasteur, Marie von Manassein, Adolf Mayer, Nägeli and Loew). A slight modification of the grinding processes which had been used by several of these authors, led, however, to success. Hans and Eduard Buchner applied to yeast the process of grinding with sand which they had previously employed successfully for bacteria. By adding kieselguhr, at the suggestion of Hahn, to the pasty mass obtained, and submitting the mixture to a high pressure, they obtained a clear liquid which was capable of fermenting sugar (Buchner, Ber. 1897, **30**, 117).

THE NATURE OF THE ACTIVE AGENT IN YEAST JUICE.—Buchner at once established the facts that the yeast juice, prepared as described, was capable in the absence of yeast cells of producing alcoholic fermentation, and that this property was still retained after the addition of chloroform, benzene or sodium arsenite, by precipitation with alcohol, by evaporation to dryness at 30–35°, or by filtration through a Berkefeldt candle, whereas it was completely destroyed at 50°. He therefore concluded that the fermentative power of the juice was due to a dissolved substance of the nature of an enzyme to which he gave the name of *zymase*. Several of the properties of this liquid, however, suggested to various investigators that it did not contain an enzyme of the ordinary kind, but rather fragments of the living protoplasm of the yeast, which retained for some time the functions which they had possessed in the cell. This idea was in harmony with the facts that the fermenting power of the juice was rapidly lost on preservation, and that comparatively large amounts of certain antiseptics did undoubtedly greatly diminish its activity. Other objections, founded on the behaviour of the juice on dilution, etc., proved not to be well founded. Further experience of the nature of yeast juice has shown that this idea has little to recommend it, and there seems at present no reason to doubt the existence of this enzyme in yeast juice.

PREPARATION AND PROPERTIES OF YEAST JUICE.—Fresh brewery yeast is washed and pressed out at about 50 kg. per sq. cm. The resulting mass, which contains about 70% of water, is mixed with an equal weight of sand, and from 0·2–0·3 part of kieselguhr, care being taken that this is free from acid. The dry powder thus formed is then ground in small portions at a time in a large porcelain mortar by means of a heavy pestle, until the mass becomes pasty, which occurs after about 1–2 minutes' grinding. The grinding may also be done in a mixing mill. The paste is then either directly pressed out after being wrapped in a filter cloth, the pressure being gradually raised to 90 kg. per sq. cm. (Buchner), or is mixed with more kieselguhr and the dry powder pressed out between layers of chain cloth (Macfayden, Morris and Rowland). A more active juice is usually obtained from English top yeasts if the ground mass be kept for 2 hours at air temperature before it is pressed out (Harden and Henley, Biochem. J. 1927, **21**, 196).

The yield of juice obtained from 1,000 g. of bottom yeast (Buchner) is about 320–460 c.c.; that obtained from English top yeasts is rather smaller, averaging 250 c.c. (Harden and Young). The product, after any suspended yeast cells have been removed by filtration or centrifuging, is a slightly viscid, brownish-yellow, opalescent, faintly acid liquid of sp.gr. 1·03–1·06. It contains about 8·5–14% of dissolved solids, and 0·7–1·7% of nitrogen, nearly all in the form of protein, so that the liquid coagulates when heated. The ash amounts to 1·4–2% and, like that of yeast, contains a large proportion of phosphoric oxide.

An active extract, known as maceration extract, has been obtained by von Lebedev (Compt. rend. 1911, **152**, 49; Ann. Inst. Pasteur, 1912, **26**, 8) by drying yeast at 25–30°, and then macerating the dried material with 3 parts of water for 2 hours at 35°. The liquid is then filtered or centrifuged and a clear active extract is thus obtained. Bottom yeasts in general give good results, whereas with some other yeasts, and notably with many English top yeasts, the process fails. In such cases better results are often obtainable by macerating with 0·15*M* K_2HPO_4 or Na_2HPO_4 (Hägglund and Rosenqvist, Biochem. Z. 1927, **180**, 61). The yeast in use in Stockholm also yields a Lebedev extract which has very feeble fermenting powers (von Euler and Adler, Z. physiol. Chem. 1934, **226**, 206). The extract closely resembles yeast juice obtained by grinding, but usually contains a larger amount of inorganic phosphate and a much smaller amount of glycogen, and often shows a long period of induction before the fermentation of added sugar begins.

When the juice is preserved, the protein becomes hydrolysed owing to the presence of a powerful proteolytic enzyme. At the same time, the power of producing alcoholic fermentation is lost, and it seems probable that this is due to the action of the proteolytic enzyme on the enzymes of fermentation (Buchner). When excess of sugar is added and the mixture incubated at 25°, a steady fermentation ensues, carbon dioxide being evolved and alcohol produced in nearly the theoretical ratio, at a rate which gradually decreases until the process stops, after 72–96 hours, not from exhaustion of the sugar, but owing to the destruction of the active agent of fermentation. In some cases (juice from bottom yeasts) the co-zymase (p. 15) is destroyed before the apo-enzyme and renewed fermentation occurs when co-zymase is added. The juice from bottom yeasts appears to be more stable and to produce a somewhat greater total fermentation than that from top yeasts, 25 c.c. of juice producing on the average at 25° an evolution of about 1–1·5 grams of carbon dioxide in the case of bottom yeast, and 0·5–1 g. in the case of top yeast.

The juice ferments those sugars which are fermentable by the yeast from which it is prepared and, in addition, dextrin, soluble starch, and glycogen, the first of which is only slowly and imperfectly fermented by yeast, and the last two not at all, as already explained. Maltose and cane sugar are hydrolysed before being fermented, and the fermentation proceeds as with the simple sugars, glucose, fructose, and mannose. Slight differences between the rates of fermentation and the total fermentations produced with these three sugars, have been observed by Harden and Young. A yeast, which ferments galactose, yields a juice which also ferments this sugar, but the action is often much less pronounced relatively to that on glucose than is that of the living yeast (Harden and Norris; *see also* Grant, Biochem. J. 1939 **29**, 1661).

Yeast juice, like living yeast, exhibits the phenomenon of autofermentation, which is carried out at the expense of the glycogen present. A diastatic enzyme, capable of hydrolysing glycogen, exists in the juice (*glycogenase*), but it seems probable (*see below*) that the glycogen is fermented without preliminary hydrolysis to glucose. Added glycogen is also fermented, but usually at a lower rate and with a smaller total yield of gas than glucose. The autofermentation of the juice from top yeast is often very considerable in amount, and may even occasionally equal that produced with glucose, whilst it is less pronounced with juice from bottom yeast. Maceration juice is almost free from autofermentation (*see* Oppenheimer, Z. physiol. Chem. 1914, **89**, 63).

The rate of fermentation of sugar varies with the concentration of the sugar in the manner characteristic of enzymes, and in this respect the juice closely resembles living yeast. After a certain small limit of concentration is attained, the initial rate is practically independent of the concentration of the sugar, but decreases slightly as this increases. The gradual destruction of the enzymes produces a gradual fall in rate which simulates the course of a unimolecular reaction, and has been regarded by some investigators as evidence that the reaction is of this type (von Euler, *ibid.* 1905, **44**, 53). Increased concentration of the sugar also increases both the duration of fermentation and the total fermentation, probably owing to a protective action on the fermenting mechanism. The rate of fermentation is diminished by dilution, and, with juice of high fermenting power, is probably proportional to the concentration of juice. The total fermentation produced is, at the same time, slightly diminished.

Accompanying the decomposition of the sugar into carbon dioxide and alcohol, a synthetic action proceeds, by which a portion of the glucose is converted into a polysaccharide, which is reconverted into glucose by hydrolysis with acid (*see* Naganishi, Biochem. J. 1926, **20**, 856). Hence the observed loss of sugar as estimated by reducing power is usually considerably greater than the sum of the weights of alcohol and carbon dioxide produced. (This phenomenon is, however, differently interpreted by von Euler; *see* Harden and Young, *ibid.* 1913, **7**, 630, where the subject is discussed.) The exact nature of this complex saccharide has not yet been determined, but observations by Cremer (Ber. 1899, **32**, 2062) point to the possibility of the synthetic production of glycogen in yeast juice. As already mentioned, succinic acid and fusel oil are not formed by yeast juice, whereas glycerol is produced to the extent of about 3·8% of the sugar fermented.

The action of antiseptics on yeast juice has been investigated in some detail. Saturation with chloroform or toluene or the addition of 1% of thymol has practically no effect, whilst the inhibiting action of substances like phenol, formaldehyde, benzoic acid and salicylic acid is very small in 0·1% solution, more considerable in more concentrated solutions. The fermenting power is destroyed by 4% chloral, 1·2% phenol, 2% sodium fluoride, 0·55% ammonium fluoride, or 1·2% hydrocyanic acid; but in this last case it is restored when the hydrocyanic acid is removed by a current of air. The action of potassium arsenite is somewhat complex, and is treated later.

Fermentation by Dry Preparations of Yeast and Yeast Juice. Yeast juice can be evaporated to dryness at 37° without loss of fermenting power as measured by the total fermentation produced. When the juice is brought into 10 vol. of acetone and rapidly drained, washed with ether, and dried, a white powder is obtained which is almost completely soluble in dilute glycerol, and retains the fermenting power of the original juice. Dry preparations can also be obtained from yeast without any previous grinding, either by drying the yeast in air, preferably at 37°, or by treating it twice with a large volume of acetone (or alcohol and ether), washing with ether and drying. The material prepared in the latter way amounts to about 30% of the pressed yeast taken, and is known as acetone yeast, permanent yeast (*Dauerhefe*) or *zymin*, and is almost anhydrous, sterile and quite incapable of growth, but readily produces alcoholic fermentation when brought into sugar solution. The general phenomena of fermentation by its means are the same as are produced by yeast juice. Both the total fermentation and the rate of fermentation are 4–6 times greater than would be obtained with the yeast juice prepared from the same weight of yeast.

The Conditions of Action of the Fermenting Agent Contained in Yeast Juice.—The investigation of the mode of action of yeast juice on sugar has shown that the process is very complex. A number of enzymes are concerned, some of which are readily dissociable into thermolabile apo-enzymes and thermostable co-enzymes, the presence of both of which is essential for the production of fermentation, and moreover, the chemical change is not a simple decomposition of sugar, according to Gay-Lussac's equation, but a complicated reaction in which hexose esters of phosphoric acid take part (Harden and Young, Proc. Roy. Soc. B. 1906, **77**, 405; **78**, 369; 1908, **80**, 299; 1909, **81**, 336; 1910, **82**, 321), and in which a number of phosphorylated 3-carbon compounds are formed as intermediaries.

The Co-enzymes of Alcoholic Fermentation.

I. Co-zymase (Co-dehydrogenase I).

When yeast juice is passed under pressure through a Martin filter, which consists of a Chamberland filtering candle impregnated with 7–10% gelatin, all the colloidal matter of the juice is retained on the filter, whilst the dialysable substances pass through. When these two portions, the residue and the filtrate, are separately incubated with sugar solution, it is found that neither of them is capable of producing fermentation. When, however, the two solutions are mixed, fermentation proceeds at almost the same rate as with the original yeast juice (Harden and Young, J. Physiol. 1905, **32**, Proc. of 12.11.1904; Proc. Roy. Soc. B. 1906, **78**, 369). Yeast juice, therefore, contains a dialysable substance essential for the process of fermentation, and this was provisionally termed the co-enzyme or co-ferment, and was subsequently known as co-zymase (H. von Euler and K. Myrbäck, Z. physiol. Chem. 1923, **131**, 179). It is also present in zymin, from which it can be removed by washing with water, an inactive residue being left (*see later*, p. 18).

Little progress was at first made in our knowledge of the nature and functions of co-zymase and for many years almost the only facts known about it were that it was thermostable and dialysable, that it was destroyed by hydrolysis (acid or alkaline) and gradually disappeared from fermenting yeast juice, and that it was not precipitated by normal lead acetate. In 1918 Meyerhof made the important observation that co-zymase was also present in animal tissues (Z. physiol. Chem. 1918, **101**, 165; **102**, 1), which was the first step towards the discovery that the process of lactic acid formation from carbohydrate in muscle is chemically closely analogous to the fermentation of sugar by yeast (*see later*).

The idea that co-enzymes were necessary for the reducing action of yeast and its preparations was early mooted by von Lebedev and Graiznov (Ber. 1912, **45**, 3256), and was subsequently supported by von Euler and his colleagues, who also thought that a co-enzyme was concerned in the esterification of phosphoric acid (*see* von Euler and Myrbäck, Z. physiol. Chem. 1924, **139**, 15; 1927, **165**, 28). These ideas are now generally accepted (*see* Harden, "Alcoholic Fermentation," Longmans Green, 4th ed., 1932, for a more detailed discussion of these early theories).

The co-zymase of alcoholic fermentation has now been prepared from yeast in a condition approaching purity by von Euler (*see* von Euler, Albers and Schlenk, Z. physiol. Chem. 1936, **240**, 113; von Euler and Schlenk, *ibid.* 1937, **246**, 64), who with his colleagues has published a long series of papers on the subject commencing in 1924 (*see* the articles "Cozymase," by Myrbäck in Fermentforsch. 1935, **2**, 139, and by von Euler in Ergebn. Physiol. 1936, **38**, 1). It has also been prepared from red blood corpuscles by a different method by Warburg and Christian (Biochem. Z. 1936, **285**, 56; **287**, 291) and its function in fermentation has been to a considerable extent established. The attainment of this result has been greatly aided by the discovery of a second co-enzyme (Co-dehydrogenase II) by Warburg and Christian (Biochem. Z. 1931, **242**, 206), which was originally prepared from the red blood corpuscles of the horse. It also occurs in yeast, but as far as is known, plays no direct part in alcoholic fermentation (*see later under* "Phosphorylation by Co-zymase," p. 39).

This compound, which is specifically necessary for the dehydrogenation of hexosemonophosphate by yeast preparations with production of a phosphohexonic acid, was recognised (Warburg, Christian and Griese, Biochem. Z. 1935, **282**, 157) as a triphosphodinucleotide derived from adenine, the amide of nicotinic acid and two molecules of ribose. Its function as a co-dehydrogenase was traced to the fact that the pyridine ring of the nicotinamide residue is capable of combining reversibly with two atoms of hydrogen.

Co-zymase was shortly after this recognised as a closely allied substance, a diphosphodinucleotide also derived from adenine, nicotinamide and ribose (von Euler, Albers and Schlenk, Z. physiol. Chem. 1935, **237**, 1; Warburg and Christian, Biochem. Z. 1936, **287**, 291). von Euler terms these two co-enzymes, co-dehydrogenase I (co-zymase) and co-dehydrogenase II (Warburg's co-enzyme). Warburg terms them diphosphopyridinenucleotide (co-zymase) and triphosphopyridinenucleotide (Warburg's co-enzyme). Adenylpyrophosphate (adenosinetriphosphate) which was early recognised as the co-enzyme of lactic acid formation in muscle, also occurs in yeast (*see* p. 35), and is capable of playing a part in some of the stages of alcoholic fermentation in which phosphorylation and dephosphorylation occur, but cannot activate fermentation in the absence of co-zymase.

PREPARATION OF CO-ZYMASE FROM YEAST EXTRACT.—The following scheme indicates the stages by which co-zymase is obtained from yeast extract (von Euler, Albers and Schlenk, Z. physiol. Chem. 1936, **240**, 113; von Euler and Schlenk, *ibid.* 1937, **246**, 64).

The activity of the preparation (*ACo*) is given by the c.c. of CO_2 per gram of added co-zymase preparation which is evolved under fixed conditions from a mixture of washed dried yeast (apo-zymase), sugar, phosphate and hexosediphosphate, the unit (*Co*) being that weight of co-zymase which produces an evolution of 1 c.c. per hour.

	Yield in *Co.*	Average activity *ACo.*
(*a*) Hot water extract from 10 kg. baker's yeast	1,500,000	500
(*b*) Lead acetate filtrate from (*a*) .	1,350,000	5,000
(*c*) $HgNO_3$ ppt. from (*b*), decomposed with H_2S . . .	675,000	10,000
(*d*) Phosphotungstic acid ppt. from (*c*), decomposed with H_2SO_4, amyl-alcohol and ether .	435,000	35,000
(*e*) Ammoniacal $AgNO_3$ ppt. from (*d*), decomposed with H_2S	429,000	100,000
(*f*) Cuprous salt from (*e*), decomposed with H_2S, co-zymase ppted. with alcohol . . .	360,000	400,000

The product thus obtained possessed the power of acting both as a co-phosphorylase and as a co-dehydrogenase and was found to contain adenylic acid and other impurities. It is best freed from these by successive treatments with baryta and lead acetate, followed by precipitation from concentrated solution by alcohol. 1 g. of the *ACo* 400,000 product thus yields 0·25 g. of *ACo* 650,000, which no longer acts as a co-phosphorylase when tested in the ordinary way (*see later* "Phosphorylation by Co-zymase," p. 38), but retains the properties of a co-dehydrogenase. In contrast with this 1,000 litres of horse blood yield by the method of Warburg and Christian 0·93 g. co-zymase, 1·13 g. co-dehydrogenase II and 5 g. adenylpyrophosphate.

REDUCTION OF CO-ZYMASE.—The pyridine ring present as nicotinamide in codehydrogenase I and II readily takes up hydrogen under various conditions:—

1. *Reversible Combination with 2 Atoms of Hydrogen.*—The chemistry of this process was first worked out for co-dehydrogenase II (Warburg, Christian and Griese, Biochem. Z. 1935, **279**, 143; **282**, 157), and it has since been found that similar conditions apply to co-dehydrogenase I (Warburg and Christian, *ibid.*, 1936, **285**, 156; **286**, 811; **287**, 291; Adler, Hellström and von Euler, Z. physiol. Chem. **242**, 225; von Euler, Adler and Hellström, *ibid.* 1936, **241**, 239; Svensk Kem. Tidskr. 1936, **47**, 290).

(*a*) *Reduction by Hyposulphite* (hydrosulphite, $Na_2S_2O_4$).—The pyridinenucleotides take up 2 atoms of hydrogen when they are treated with $Na_2S_2O_4$ at neutral reaction.

$$\mathit{Co}+Na_2S_2O_4+2H_2O=\mathit{Co}H_2+2NaHSO_3$$

As this reaction results in the production of acid it can be used in the presence of $NaHCO_3$ for the manometric estimation of the degree and capacity of hydrogenation of the co-enzyme (Warburg, Christian and Griese, *l.c.*).

The resulting compound ($\mathit{Co}H_2$) is identical with that obtained enzymically (*see later*) and is stable in the air, so that when the $NaHSO_3$ is oxidised by a current of air the $\mathit{Co}H_2$ remains almost unchanged, but undergoes a slow re-oxidation at a rate dependent on the p_H. The two hydrogen atoms are, however, rapidly removed when the $\mathit{Co}H_2$ (however prepared) is exposed to oxygen and a suitable oxygen carrier (*see later*, p. 34).

An unstable yellow intermediate compound, probably monohydro-co-zymase (Hellström, Z. physiol. Chem. 1937, **246**, 155), is formed during the reduction of co-zymase by $Na_2S_2O_4$. It is only stable in alkaline solution and is much more readily oxidised than $\mathit{Co}H_2$ (Adler, Hellström and von Euler, Z. physiol. Chem. 1936, **242**, 225).

(*b*) *Enzymic Reduction.*—Co-zymase can be reduced enzymically in several different reactions: (*a*) the dehydrogenation of alcohol; (*b*) the dehydrogenation of phosphotriose (von Euler, Adler and Hellström, Z. physiol. Chem. 1936, **241**, 239); (*c*) the dehydrogenation of hexosemonophosphate, with indirect production of pyruvic acid (Warburg and Christian, Biochem. Z. 1936, **287**, 291); (*d*) the dehydrogenation of lactic acid (Meyerhof and Ohlmeyer, Naturwiss. 1936, **24**, 741; von Euler, *et al.* Arkiv. Kemi, Min., Geol. 1936, **12B**, Nos. 24 and

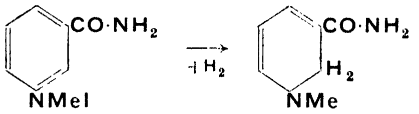
25) provided that in all cases the proper "apo-dehydrogenase" is present. The mechanism of these changes is discussed later on (p. 33).

2. *Irreversible Reduction by Hydrogen in Presence of Platinum.*—At p_H 9·4 *Co* II, when treated with platinum and hydrogen, takes up 190 cu.-mm. of H_2 per mg. corresponding with 6 atoms of hydrogen for each nicotinamide group. Similarly the reversibly reduced compound takes up 4 atoms of hydrogen and these phenomena may be utilised for estimating the amount of nicotinamide present (Warburg, Christian and Griese, 1935, *loc. cit.*). The fully reduced compound is not oxidised by oxygen in presence of the yellow enzyme (Hellström, *v. s.*).

Co I behaves in this respect in a precisely similar manner to *Co* II.

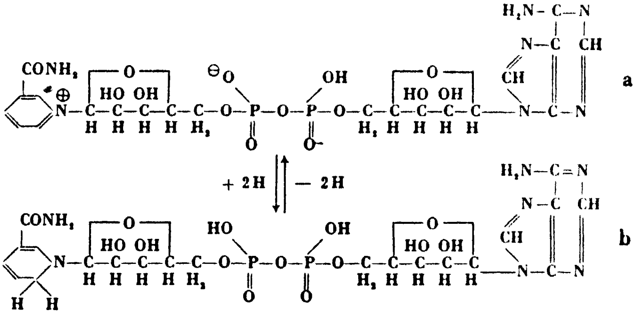
CONSTITUTION OF CO-ZYMASE AND DIHYDRO-CO-ZYMASE.—(1) *Empirical Formula from Acid Hydrolysis.*—Acid hydrolysis of co-zymase (von Euler, Albers and Schlenk, *l.c.*; *cf.* Warburg and Christian, Biochem. Z. 1936, **287**, 21) yields 1 mol. adenine, 1 mol. nicotinamide and 2 mols. ribose-5-phosphoric acid (von Euler, Karrer and Beck, Helv. chim. Acta, 1936, **19**, 1060), the condensation of which with loss of 5 mol. water leads to the empirical formula $C_{21}H_{27}O_{14}N_7P_2$, which has been substantiated by elementary analysis (von Euler and Schlenk, Svensk Kem. Tidskr. 1936, **48**, 135).

(2) *Structural Formula.*—The reduction of various derivatives of nicotinamide has been studied by Karrer *et al.* (Helv. Chim. Acta, 1936, **19**, 811), with the result that the only one which was found to behave like co-zymase was the quaternary methiodide. The pyridine group of co-zymase, is therefore probably present as a pyridinium base.



In agreement with this result and with the results obtained by hydrolysis, the following formulæ have been proposed (Schlenk, *et al.*, *l.c.*; *see also* Vestin, Schlenk and von Euler, Ber. 1937, **70** [B], 1369).

Co-zymase



Dihydro-co-zymase

According to this co-zymase is a dinucleotide of adenine and nicotinamide, the two mononucleotide groups being united through a pyrophosphoric acid group, the presence of which is proved by the production of adenosinediphosphoric acid by alkaline hydrolysis.

The carbohydrate portion of the molecule is derived from ribose-5-phosphoric acid and in the adenine nucleotide this is combined with the N-atom in position 9 (*see* Gulland and Holiday, J.C.S. 1936, 765).

PROPERTIES OF CO-ZYMASE.—(1) *Optical Properties* (*see* Warburg and Christian, Biochem. Z. 1936, **286**, 81; **287**, 291; von Euler, Alder and Hellström, Z. physiol. Chem. 1936, **241**, 239).

Both *Co* I and *Co* II show an absorption band in the ultra-violet at 260 mμ, which is due to the adenine and pyridine groups. When the co-dehydrogenases are reduced, either chemically or enzymically, this band diminishes in intensity and a new band develops at 340 mμ which is accompanied by a brilliant white fluorescence. The spectra of *Co* I and *Co* II are closely similar and the "reduction" band has its maximum at the same wave-length (340 mμ) in both cases.

(2) *Stability to Acid and Alkali.*—Whereas the unreduced co-dehydrogenases are stable in acid and unstable in alkaline solution (0·1 *N*-NaOH inactivates them with loss of the nicotinamide group in one hour at room temperature) the relations are exactly reversed with the reduced compounds. These are stable to 0·1 *N*-NaOH (co-zymase can be boiled with 0·1 *N*-NaOH without undergoing change, von Euler), and are to a large extent inactivated on acidification.

(3) *Products of Alkaline Hydrolysis.*—Alkaline hydrolysis produces nicotinamide and a number of other products (Schlenk, *et al.* Z. physiol. Chem. 1937, **247**, 23; Vestin and von Euler, *ibid.* 1937, **247**, 43; Vestin, Schlenk and von Euler, Ber. 1937, **70** [B], 1369) from which adenosinediphosphoric acid (*see later*) has now been isolated. This substance is capable of acting

as a co-phosphorylase (p. 38) in a similar manner to adenylpyrophosphate.

(4) *Electrometric Titration.*—When titrated electrometrically co-zymase behaves as a monobasic acid (von Euler and Schlenk, Z. physiol. Chem. 1937, **246**, 64).

(5) *Reduction of Alkaline Hypoiodite.*—*Co* I has strong reducing properties. When treated with alkaline hypoiodite it reduces the equivalent of 6 atoms of iodine (Myrbäck, Z. physiol. Chem. 1935, **242**, 225). The nature of this reaction is unknown, but it is probably connected with oxidation of the nicotinamide group (Karrer, Schlenk and von Euler, Arkiv. Kemi, Min., Geol. 1936, 12B, No. 26, 1).

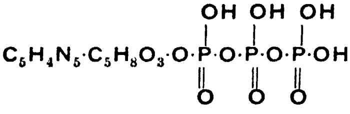
After being heated with 0·03 *N*-NaOH for a few minutes it reduces only 2 atoms of iodine. This is probably due to the oxidation of an aldehyde group unmasked by removal of the pyridine group. After acid hydrolysis it reduces 4 atoms of iodine, a second aldehyde group having been unmasked by removal of the adenine group (von Euler and Schlenk, Svensk Kem. Tidskr. 1936, **48**, 135).

NATURAL OCCURRENCE.—It is theoretically probable that *Co* and *Co*H_2 exist together in equilibrium in cells and cell preparations and their reactions with acids and alkalis have been applied to the determination of the proportions of the two substances actually present (Adler and von Euler, Svensk Kem. Tidskr. 1936, **48**, 221).

The principle of the method is that extraction with dilute acid gives the unreduced (acid-stable) *Co*, whilst extraction with 0·01 *N*-alkali gives the reduced (alkali-stable) *Co*H_2.

Preliminary experiments indicate that the ratio *Co*/*Co*H_2 in baker's yeast is about 2, in dried bottom yeast 18–19 and in maceration extract about 1.

II. **Adenylpyrophosphate** (adenosinetriphosphate) and its derivatives.—It was first shown by Lohmann (Biochem. Z. 1931, **241**, 50) that the readily dialysable co-enzyme of lactic acid formation in muscle extract consisted of two parts: (*a*) magnesium; (*b*) adenylpyrophosphate. Adenylic acid itself is a nucleotide derived from adenine, ribose and phosphoric acid and is found in muscle combined with a pyrophosphoric group forming adenylpyrophosphate, for which Lohmann suggests the formula (Biochem. Z. 1935, **282**, 120).



$$\mathrm{C_5H_4N_5{\cdot}C_5H_8O_3{\cdot}O{\cdot}\underset{\overset{\|}{O}}{\overset{\underset{|}{OH}}{P}}{\cdot}O{\cdot}\underset{\overset{\|}{O}}{\overset{\underset{|}{OH}}{P}}{\cdot}O{\cdot}\underset{\overset{\|}{O}}{\overset{\underset{|}{OH}}{P}}{\cdot}OH}$$

Adenine. Ribose. Phosphoric acid. Pyrophosphoric acid.

It acts (in presence of the specific apo-enzyme) as a co-phosphorylase by losing PO_4 to some acceptor, *e.g.* glucose or hexosemonophosphate, yielding adenylic acid, which recombines with the phosphate from some donator, *e.g.* phosphopyruvic acid.

1. Adenylpyrophosphate + hexosemonophosphate → adenylic acid + hexosediphosphate.
2. Adenylic acid + phosphopyruvic acid → adenylpyrophosphate + pyruvic acid.

Under suitable enzymic conditions only one PO_4 group is removed and adenosinediphosphoric acid is formed, which acts as a co-phosphorylase in a similar manner to adenylic acid. Adenylic acid (adenosinemonophosphate) may also act as a PO_4 donator yielding adenosine, which acts as a PO_4 acceptor. The formation of these substances is discussed later on (p. 37).

III. **Magnesium ions.**—Mg^{++} appears to be necessary both for lactic acid formation in muscle and for the fermentation of sugar by yeast. It cannot be removed from zymin or dried yeast by washing with water, which removes adenylpyrophosphate and co-zymase, but it is removed when the washing is effected with $\mathrm{KH_2PO_4}$ solution. It appears to be necessary for phosphorylation but not for the action of the dehydrogenases.

IV. **Manganese ions.**—Mn^{++} appears also to be essential either alone or in conjunction with Mg^{++} for the attainment of a maximum rate of phosphorylation, the concentration required being about 0·001% (Ohlmeyer and Ochoa, Naturwiss. 1937, **25**, 253). There is still some doubt (*see* p. 38) as to the function of both Mg and Mn (*see idem*, Biochem. Z. 1937, **293**, 338).

V. **Co-carboxylase.**—Washed zymin readily decomposes pyruvic acid (Harden, Biochem. J. 1913, **7**, 214; Neuberg and Rosenthal, Biochem. Z. 1913, **51**, 128), but a co-carboxylase is present. This can be removed from zymin by washing with a phosphate solution at p_H 7·8 or from maceration extract by dialysis against $\mathrm{Na_2HPO_4}$ solution (Auhagen, Z. physiol. Chem. 1931, **204**, 149; 1932, **209**, 2). Co-carboxylase has been isolated from bottom yeast in the crystalline form (Lohmann and Schuster, Naturwiss. 1937, **25**, 26; Biochem. Z. 1937, **294**, 188), and according to these authors is a pyrophosphoric ester of vitamin B_1, the hydrochloride having the formula

$$\mathrm{C_{12}H_{21}O_8N_4P_2SCl}$$

It has been synthesised chemically in small yield by the action of $\mathrm{POCl_3}$ on the vitamin (Stern and Hofer, Science, 1937, **85**, 483) and enzymically by the action of dried yeast (washed free of co-carboxylase) or of the duodenal mucosa of the pig on a mixture of vitamin B_1 and phosphate at p_H 6·7–6·8 (Tauber, Science, 1937, **86**, 180; *see also* von Euler and Vestin, Naturwiss. 1937, **25**, 416; Peters, Biochem. J. 1937, **31**, 2240).

The orthophosphoric mono-ester, produced by acid hydrolysis, has no co-enzymic activity.

INACTIVATION OF ZYMIN AND DRIED YEAST BY WASHING.

When dried yeast or zymin is washed with water several stages of inactivation can be distinguished, the most important of which are the following (*see* Stheeman, Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 426 (No. 4); 1930, **33**, 889):—

(1) The residue produces no fermentation with glucose (or fructose) and phosphate, but can be reactivated by hydrogen acceptors: *e.g.* ketonic acids (Neuberg and Schwenk, Biochem. Z. 1913, **71**, 135), aldehydes (Harden, Biochem. J. 1917, **11**, 64), methylene blue (Stheeman).

(2) A stage is reached at which hexosediphosphate can be fermented, but not the hexoses even in presence of phosphate (*see* Meyerhof, "Die chemischen Vorgänge im Muskel," 1930, p. 163).

(3) After still more thorough washing the residue requires for activation: (*a*) a hydrogen acceptor, (*b*) hexosediphosphate, and (*c*) co-zymase. If a comparatively large quantity of co-zymase is present, hexosediphosphate is not required.

(4) If the preparation be washed with a solution of KH_2PO_4 the magnesium is removed and such a residue cannot be activated unless a magnesium salt be also added.

(5) Finally, washing with alkaline phosphate removes the co-carboxylase (p. 18). To ferment sugar such a preparation requires hexosediphosphate, adenylpyrophosphate, co-zymase, co-carboxylase and a Mg salt (Lohmann and Schuster, Biochem. Z. 1937, **294**, 188).

The Function of Phosphates in Alcoholic Fermentation.—The addition of a soluble phosphate to a fermenting mixture of yeast juice or maceration extract and sugar produces a remarkable effect. The rate of fermentation is greatly increased, gradually attains a maximum, and remains at this high value for a certain time, after which it rapidly falls until it is again approximately the same as before the addition of phosphate. During this period of enhanced fermentation, the amounts of carbon dioxide and alcohol produced exceed those which would have been formed in the absence of added phosphate by an amount exactly equivalent to the phosphate added in the ratio $R_2HPO_4:CO_2+C_2H_6O$ (Harden and Young, Chem. Soc. Proc. 1905, **21**, 189). The phosphate is, at the same time, converted into a mixture of phospho-organic compounds the phosphorus of which is not precipitated by magnesium citrate mixture or uranium salts (Harden and Young; Ivanov, Z. physiol. Chem. 1907, **50**, 281).

It was at first thought that only one phosphoric ester was formed, hexosediphosphate, $C_6H_{10}O_4(PO_4H_2)_2$, and the reaction which occurred was formulated:

$$(1)\quad 2C_6H_{12}O_6+2R_2HPO_4 \rightarrow C_6H_{10}O_4(PO_4R_2)_2+2CO_2+2C_2H_6O+2H_2O$$

It was subsequently found that a mixture of hexosemonophosphoric esters $C_6H_{11}O_5(PO_4H_2)$ was also produced (Harden and Robison, Proc. Chem. Soc. 1914, **30**, 16; Robison, Biochem. J. 1922, **16**, 809) according to the empirical equation (Harden and Henley, Biochem. J. 1927, **21**, 1216; 1929, **23**, 230):

$$(1a)\quad 3C_6H_{12}O_6+2R_2HPO_4 \rightarrow 2C_6H_{11}O_5(PO_4R_2)+2CO_2+2C_2H_6O+2H_2O$$

It is a remarkable fact that, as the result of adding phosphate, the molecular ratio of the CO_2 produced to the phosphate esterified remains approximately constant and equal to unity whatever the relative proportion of monophosphoric and diphosphoric ester produced (Harden and Henley, *l.c.*; Robison and Morgan, *ibid.* 1930, **24**, 119; *see also* Kluyver and Struyk, Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 882) (*see later*, p. 30).

The proportions in which the mono- and diphosphoric esters are produced vary considerably with the nature of the yeast preparation and are influenced by factors not yet properly understood. Thus yeast juice and maceration extract may produce monophosphoric ester varying in amount between 10 and 80% of the phosphate esterified; dried yeast and zymin usually produce about 10–30% of monophosphoric ester. The mechanism of this reaction is discussed later on.

In presence of excess of sugar the esterification proceeds according to a unimolecular reaction, and is most rapid at a faintly alkaline reaction (von Euler and Kullberg, Z. physiol. Chem. 1911, **74**, 15).

The existence of this reaction rendered it probable that phosphates were essential for the alcoholic fermentation of the sugars by yeast juice and that in their absence no fermentation would occur. This conclusion has been confirmed in a very striking manner by experiment. A mixture of enzyme, co-enzyme, and sugar can be prepared which contains no more than traces of free phosphate or hexosephosphate and very little phosphorus in any form which can yield phosphate by enzymic action. Such a mixture is almost completely devoid of fermenting power, but ferments readily when a small proportion of phosphate is added. In a particular case, the phosphate-free mixture only gave 1·5 c.c. of carbon dioxide, whereas in presence of phosphate 132 c.c. were produced (Harden and Young, Proc. Roy. Soc. 1911, B, **83**, 451). As the result of the reaction expressed by equations (1) and (1a) practically the whole of the free phosphate of the juice is converted into hexosephosphates and the fermentation should therefore come to a close unless some means of regeneration of free phosphate were provided. It was thought at the time that the necessary phosphate was supplied by the hydrolysis of the hexosephosphate, which is effected by an enzyme, termed *hexosephosphatase*, and yields a hexose and a phosphate:

$$(2)\quad C_6H_{10}O_4(PO_4R_2)_2+2H_2O = C_6H_{12}O_6+2R_2HPO_4$$

both the hexose and the phosphate thus formed entering again into reaction (1). It now appears that this reaction is only of subsidiary importance and that the hexosediphosphate is fermented without preliminary hydrolysis (*see later*, p. 21).

It is now possible to understand the conditions which prevail in yeast juice fermenting glucose in the presence or absence of added phosphate. When the proper or optimum amount of phosphate is added, reactions 1 and 1a proceed at the maximum rate, and this rate affords a measure of the concentration of the fermenting complex present in the juice. When all the phosphate has been converted into hexosephosphates the rate falls to a low level, the so-called normal or basal rate of fermentation, which represents the rate of fermentation of a mixture of hexosephosphate and glucose in absence of inorganic phosphate.

Several minor points remain for consideration with regard to the action of phosphate. In the first place, phosphate not only sets up a temporarily enhanced fermentation, but also considerably increases the total fermentation produced, apparently by means of a protective action of the hexosephosphate on the various enzymes concerned. Excess of phosphate produces a secondary inhibiting effect, and may lead to a diminished fermentation instead of an enhanced fermentation. Excess of arsenate and arsenite produces similar effects but are much more marked in their action, often leading to total inhibition. A similar effect is produced by many other salts (Meyerhof, Z. physiol. Chem. 1918, **102**, 185), so that the phosphate exerts both a specific action and a general salt-effect: *see* Harden and Henley (Biochem. J. 1921, **15**, 312).

Fructose produces a much greater rate of fermentation in presence of phosphate than does glucose, and the optimum concentration of phosphate is greater in presence of fructose than in presence of glucose, as shown by the following numbers referring to 10 c.c. of yeast juice :—

Optimum concentration of phosphate in terms of a molar solution		Maximum rate of fermentation in c.c. of CO_2 per 5 minutes	
Glucose	Fructose	Glucose	Fructose
0·034	0·085	7·5	32·2
0·012	0·120	5·4	28·4
0·026	0·130	8·0	17·0
0·120	0·180	16·2	31·2

Zymin and dried yeast also react with phosphate in a similar manner to yeast juice, but the rate is not so greatly increased, and the effects are not so marked.

Effect of Arsenate.—When Na arsenate is added to a fermenting mixture of yeast juice and sugar, the rate of production of CO_2 and alcohol is greatly increased, the maximum rate in presence of the optimum concentration of arsenate (about 10^{-3} *M*) being 5–10 times the normal and of the same order as the maximum attainable with phosphate (Harden and Young, Proc. Chem. Soc. 1906, **22**, 283; Proc. Roy. Soc. 1911, **83**B, 451). This high rate continues for a considerable time and there is no equivalence between the extra amount of CO_2 evolved and the arsenate added, there is no accumulation of hexosephosphates, nor has any hexosearsenic ester been isolated (*cf.* Braunstein, Biochem. Z. 1931, **240**, 68; *ibid.* 1934, **271**, 285; Braunstein and Levitov, *ibid.* 1932, **252**, 56). A similar but less marked effect is caused by arsenite. The effect has been traced to a specific acceleration of the rate of fermentation of hexosediphosphate (*see* p. 39). Arsenate does not accelerate the fermentation of hexosemonophosphate.

The Hexosephosphates of Fermentation.

The product of fermentation of the hexoses, glucose, fructose, mannose and galactose by yeast preparations in presence of inorganic phosphate is a complicated mixture containing a number of hexosephosphoric esters, and all these sugars appear to yield the same products. There are present, in addition to hexosediphosphate, a mixture of the monophosphoric esters of glucose, fructose and mannose (Robison, Biochem. J. 1922, **16**, 809; 1932, **26**, 2191; Robison and Morgan, *ibid.* 1930, **24**, 119; Robison and King, *ibid.* 1931, **25**, 323), sometimes, especially when dried yeast has been used, trehalosemonophosphate (Robison and Morgan, *ibid.* 1928, **22**, 1277), as well as small amounts of phosphopyruvate, triosephosphate, α-glycerophosphate, phosphoglycerate and other not yet identified constituents. The products are best separated by the method of Robison and Morgan (Biochem. J. 1930, **24**, 119) which consists in removing the yeast protein which is always present by trichloroacetic acid (4%) and then precipitating the hexosediphosphate and inorganic phosphate by barium acetate and baryta at p_H 8·4. The hexosemonophosphates and trehalosephosphate form soluble barium salts and are precipitated from the filtrate by basic lead acetate. (For other methods of extraction, *see* Robison, Biochem. J. 1922, **16**, 809; Neuberg and Leibowitz, Biochem. Z. 1927, **184**, 489).

Hexosediphosphate.—The crude barium salt obtained as described is extracted with 200 parts of cold water at p_H 8·6. The clear filtrate, which is free from inorganic phosphate, is treated with alcohol to incipient precipitation, and then heated at 70° in a water-bath. The barium salt, which is less soluble in hot than in cold water, is precipitated and is filtered off at 70° and dried at a low temperature over P_2O_5 *in vacuo*.

All the metallic salts are amorphous, and the magnesium, calcium, barium and manganese salts, which are only sparingly soluble, are more soluble in cold than in hot water, and can be purified by taking advantage of this property. The free acid has not been obtained in the pure state, but in solution is faintly dextrorotatory, $[\alpha]_D = +3·4°$. It is decomposed when boiled alone or with acids yielding phosphoric acid and fructose.

Hexosediphosphate is present in freshly prepared yeast juice, in yeast extract and in the solution obtained by adding trichloroacetic acid to actively fermenting yeast (*see* p. 40), so that it may be regarded as certain that it is present in the living yeast cell.

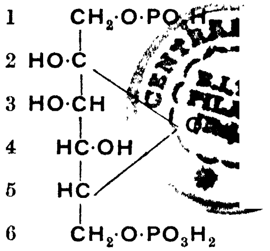
It is, however, remarkable that hexosediphosphate is not fermented by living yeast. This fact was first observed by Ivanov, and has been confirmed by Harden and Young, and by von Euler and Backström, who have also found that the hexosediphosphate accelerates the fermentation of glucose by yeast although it is not itself either hydrolysed or fermented.

Constitution of Hexosediphosphoric Ester.—Ivanov regarded this compound as a triosemonophosphoric ester, $C_3H_5O_2(PO_4H_2)$, but the evidence on which this view rests was shown to be unsatisfactory. von Lebedev, on the other hand, at first regarded it as a hexosemonophosphoric ester, basing this view solely on the composition of the phenylhydrazine derivative,

$$C_6H_5NH{\cdot}NH_2,H_2PO_4CH_2{\cdot}[CH{\cdot}OH]_3{\cdot}\\ C(N_2C_6H_6)CH(N_2C_6H_6)$$

which is the phenylhydrazine salt of a monophosphoric ester of hexosazone. Young, however, supported the original view of Harden and Young, which is now generally accepted, that the compound is a hexosediphosphoric ester, $C_6H_{10}O_4(PO_4H_2)_2$, since analyses of the salts agree with this formula; phosphoric acid is split off during the formation of the phenylhydrazine derivative, but a hydrazone containing two phosphoric acid groups for one molecule of hexose has been prepared.

Young concluded from his investigations that one phosphoric acid group occupied position 1 in the carbon chain of the sugar. It has now been found that on methylation the ester yields a mixture of α- and β-methylhexosediphosphoric esters which, on treatment with bone phosphatase to remove the phosphoric groups, gives rise to the corresponding α- and β-methylfructosides. These are derivatives of the γ-form of fructose (fructo-furanose), so that the ester itself must also be a derivative of this form of fructose (Morgan, Biochem. J. 1927, **21**, 675; Morgan and Robison, Biochem. J. 1928, **22**, 1270) as shown in the formula



It may be concluded from this that the second phosphoric group is in position 6, as otherwise it would be expected that the pyranose form of fructose would be obtained.

Fermentation of Hexosediphosphoric Ester.—Yeast preparations can be obtained which contain so little co-enzyme that they are no longer capable of fermenting sugars but still ferment hexosediphosphate. This led Meyerhof to the conclusion that hexosediphosphate could be directly fermented without a preliminary hydrolysis to hexose and phosphoric acid. This conclusion is confirmed by the observation (Meyerhof, Biochem. Z. 1927, **183**, 176; Raymond, J. Biol. Chem. 1928, **79**, 637; Macfarlane, Biochem. J. 1930, **24**, 1051) that in the absence of co-enzyme arsenate does not produce any acceleration in the rate of hydrolysis of hexosediphosphate. It is therefore evident that two mechanisms exist for the production of alcohol and CO_2 from hexosediphosphate: (1) hydrolysis to hexose and phosphoric acid, followed by fermentation accompanied by partial re-esterification of the sugar; (2) direct fermentation without preliminary hydrolysis; this is the process which is accelerated by arsenate (*see* p. 39). This second process requires the presence of co-enzyme, but in much smaller concentration than is needed for the first process. In the fermentation of sugars by yeast preparations these reactions probably occur simultaneously and are jointly responsible for the regeneration of phosphoric acid, but the greater part of the change is due to direct fermentation.

Hexosemonophosphoric Esters.—For the further purification of these the basic lead salts obtained as described above (p. 20) are reconverted into barium salts which can be precipitated from aqueous solution by alcohol. The resulting product (Robison, Biochem. J. 1922, **16**, 809; Robison and Morgan, Biochem. J. 1930, **24**, 119; Robison and King, J.S.C.I. 1929, **48**, 14; Biochem. J. 1931, **25**, 323) is a mixture which has not yet been completely resolved, but the substances described below have so far been isolated from it, mainly by fractional crystallisation of the brucine salts.

(1) An aldose ester, *glucose-6-phosphoric ester*, the brucine salt of which is only sparingly soluble in methyl alcohol. The reducing power of the barium salt to alkaline hypoiodite corresponds to that of the glucose contained in it, whilst to Hagedorn and Jensen's reagent it is about 78% of this. $[\alpha]_{5461}$ is $+20{\cdot}6°$ for the barium salt, $+41{\cdot}4°$ for the free acid. It is very resistant to hydrolysis by acid, apparently yielding *d*-glucose. Bone phosphatase hydrolyses it with formation of both glucose and fructose. Bromine oxidises it to a phosphogluconic acid, which is converted by phosphatase into *d*-gluconic acid. It yields the same phospho-osazone as hexosediphosphoric ester and Neuberg's monophosphoric ester and, therefore, contains the phosphoric group in the same position (probably 6) as these compounds.

(2) A second aldose ester, *mannosemonophosphoric ester* (Robison, Biochem. J. 1932, **26**, 2191). The $[\alpha]_{5461}$ of the barium salt is $+3{\cdot}5°$, of the free acid $+15{\cdot}1°$, it yields a characteristic hydrazone and the same phenylosazone as that obtained from glucose- and fructose-monophosphoric esters and hexosediphosphoric ester. It is therefore probably *d*-mannose-6-phosphoric ester.

(3) A ketose ester, probably identical with the main constituent of Neuberg's ester (*fructofuranose-6-phosphoric ester*). This is obtained from the more soluble fraction of the brucine salt, by precipitation of the barium salt, after oxidation of any of the aldose constituent which may still be present by means of bromine and barium carbonate.

(4) In addition to the foregoing the presence of compounds of a different type is also indicated. When dried yeast, or bottom yeast in presence of toluene (Veibel, Z. physiol. Chem. 1931, **139**, 350) (but not yeast juice) is used for the fermentation a certain amount of *trehalosemonophosphoric ester* is produced (Robison and Morgan, Biochem. J. 1928, **22**, 1277). The barium salt of this is prepared from the most soluble fraction of the mixed barium salts and is finally obtained in the crystalline form by precipitation with alcohol. It has no reducing power; $[\alpha]_{5461}$ is $+132°$ for the barium salt, $+185°$ for the free acid. Bone phosphatase hydrolyses it to trehalose. Hydrolysis with acid yields glucose and a glucosemonophosphoric ester, the constitution of which has not yet been determined. The ester is fermented by yeast preparations.

(5) Another interesting substance, present to the extent of 1–2% in the crude hexosemonophosphate, gives a green coloration when treated with orcinol and hydrochloric acid identical with that given by the mannoketoheptose isolated from the Avocado pear by La Forge (J. Biol. Chem. 1917, **28**, 511). The

constitution of this new ester and that of the non-fermentable reducing sugar obtained from it by the action of bone phosphatase have not yet been ascertained, but the sugar is probably a mixture of a mannoketoheptose with other sugars of a similar type (Robison, Macfarlane and Tazelaar, Nature, 1938, **142**, 114).

A similar mixture of mono-esters obtained from muscle (Embden and Zimmermann, Z. physiol. Chem. 1927, **167**, 114) is known as the *Embden ester.* The phosphoric este rproduced by the action of autolysed and dialysed muscle extract on glycogen (*see* p. 36) is also of a similar character. This reaction provides a convenient method for preparing the mixed ester.

The formation of these mixtures is probably due to the presence of an enzyme (phosphohexomutase) which rapidly converts glucose-, mannose- or fructose-monophosphoric ester, probably by way of an enolic form common to all of them, into an equilibrium mixture of the three, containing about 70% aldose ester and 30% ketose ester (Lohmann, Biochem. Z. 1933, **262**, 132; Robison, Biochem. J. 1932, **26**, 2191). This mixture, originally termed the *Robison ester,* is so termed through this article, but Meyerhof suggests that it should be known as the *equilibrium ester,* and the name Robison ester reserved for glucose-6-phosphate. The fermentation of hexosemonophosphate is discussed later (*see* p. 30).

The Neuberg Ester.—An ester which is probably identical with the ketose ester described above was obtained by Neuberg (Biochem. Z. 1918, **88**, 432) by the partial hydrolysis of hexosediphosphoric ester by boiling for a short time with oxalic acid. It has $[\alpha]_D+0{\cdot}4°$ for the barium salt, $+1{\cdot}5°$ for the free acid. It reduces Hagedorn and Jensen's reagent to the same extent as the Robison ester, but only reacts to a small extent (5–10% of the hexose) with alkaline hypoiodite. This may possibly be due to the presence of some aldose ester in the material used for its preparation. It is a fructosemonophosphoric ester, which is probably *fructofuranose-6-phosphoric ester.*

A substance which is probably *fructopyranose-1-phosphoric ester* is found among the products of the action of bone phosphatase on fructosediphosphoric ester. It is strongly lævorotatory (calc. $[\alpha]_{5461}$, for **Ba** salt$=-39°$, for the free ester $-62{\cdot}2°$) and is very rapidly hydrolysed by acid; k for N-**HCl** at $100°=75\times10^{-3}$ (MacLeod and Robison, Biochem. J. 1933, **27**, 286).

Another lævorotatory fructosemonophosphate, $[\alpha]_{5461}$ $-24°$ (**Ba** salt) is formed during the acid hydrolysis of hexosediphosphate or fructosemonophosphate. Its formation is probably due to the migration of the 6-phosphoric acid group (Macfarlane and Robison, Enzymologia, 1937, **4**, 125).

An *aldose-1-phosphate* has been obtained by Cori and Cori (Proc. Soc. Exp. Biol. Med. 1936, **34**, 702; Cori, Colowick and Cori, J. biol. Chem. 1937, **121**, 465) by incubating washed minced frog muscle in phosphate buffer (*see also* Kendal and Stickland, Chem. and Ind. 1937, **56**, 936), and can also be prepared by the action of rabbit muscle extract on glycogen in presence of iodoacetic acid (Kiessling, Biochem. Z. 1938, **298**, 421), and by synthesis from acetobromoglucose (Cori, Colowick and Cori, *l.c.*). Evidence is accumulating that this substance is the first product of phosphorylation of glycogen and also that it can be enzymically reconverted into glycogen and H_3PO_4 (*see* Kiessling, Naturwiss. 1939, **27**, 129; Schäffner, *ibid.* 1939, **27**, 195). It has no reducing power (Hagedorn and Jensen; hypoiodite) and is very readily hydrolysed by acid to glucose and phosphoric acid. When added to dialysed muscle extract it rapidly passes into an equilibrium mixture of hexose-6-monophosphates (Embden ester).

The $[\alpha]_D$ for the **Ba** salt is $+75°$, for the free acid $+120°$.

HYDROLYSIS OF THE PHOSPHORIC ESTERS OF FERMENTATION.—The phosphoric acid groups of the hexosephosphoric esters, adenylic acid, adenylpyrophosphate, phosphoglyceric acid, phosphopyruvic acid, etc., are removed by hydrolysis with acid, according to a unimolecular law, at different rates, and this fact has been utilised for analytical purposes as well as for the identification of the various compounds. In practice the hydrolysis is carried out with N-**HCl** in a sealed capsule at 100° for a fixed time and the amount of inorganic phosphate liberated is then estimated (*see* Lohmann, Biochem. Z. 1928, **194**, 306). Velocity constants of the hydrolysis of a number of these compounds, are given below.

	$k\times10^3$
Hexosediphosphate. First group .	22·0
Second ,, .	4·2
Hexosemonophosphate (Robison ester)	0·2
Neuberg ester (fructose 6-phosphate)	4·36
Glucose-6-phosphate	0·26
Mannose-6-phosphate	0·29
Fructofuranose-1-phosphate . . .	75
Phosphoglyceric acid	0·14
Adenylic acid	2·3
Adenylpyrophosphate.	250
Phosphodihydroxyacetone . . .	33·7
Phosphoglyceraldehyde	37·5
Glucose-1-phosphate	200

APPARENT DISSOCIATION CONSTANTS OF THE HEXOSEPHOSPHATES.—The hexosephosphates produced in alcoholic fermentation are stronger acids than phosphoric acid and their formation is therefore accompanied by a fall in the p_H of the solution. The dissociation constants are:

	p_{K_1}	p_{K_2}
1. Phosphoric acid [1]	1·99	6·81
Hexosemonophosphate:		
Neuberg ester [2]	0·97	6·11
Embden ester [3]	—	6·12
Robison ester [3]	0·94	6·11
Hexosediphosphate:		
Harden and Young ester [1] .	1·48	6·29
Harden and Young ester, 1st group [1]	—	(6·1)
Harden and Young ester, 2nd group [1]	—	(6·5)
Glucose-1-phosphate [4] . . .	1·11	6·13

[1] Meyerhof and Suranyi, Biochem. Z. 1926, **178**, 427.

[2] Irving and Fischer, Proc. Soc. Exp. Biol. Med. 1927, **24**, 559.

[3] Meyerhof and Lohmann, Naturwiss, 1926, **14**, 1277.

[4] Cori, Colowick and Cori, J. Biol. Chem. 1937, **121**, 465.

The Chemical Changes Involved in Alcoholic Fermentation.

Many theories have been advanced suggesting various stages in the course of the decomposition of glucose to the final products—alcohol and carbon dioxide. Baeyer, in 1870, pointed out that the alternate removal and re-addition of the elements of water might lead to an accumulation of oxygen on certain of the carbon atoms, and thus render the rupture of the carbon chain possible. Wohl (Z. angew. Chem. 1907, **20**, 1169) proposed a modification of this idea, which leads to the supposition that loss of water and intramolecular change result in the formation of a ketoaldehyde which undergoes hydrolysis to methylglyoxal and glyceraldehyde; the latter of which, by a similar series of changes, also forms methylglyoxal,

$$CH_3{\cdot}CO{\cdot}CHO.$$

This then passes into lactic acid, and this into carbon dioxide and alcohol. This theory received a certain amount of experimental support from the fact that small quantities of lactic acid appear to be fermented by yeast juice (Buchner and Meisenheimer, Z. wiss. Landwirtschaft. 1909, **38**, 265). The idea of the occurrence of lactic acid as a true intermediate product of alcoholic fermentation has, however, now been abandoned, largely owing to the criticisms of Slator, who pointed out that this substance should be fermented at least as quickly as glucose, and that this is not the case. The same criticism is valid against many of the 3-carbon compounds which have been proposed as intermediate products, including glyceraldehyde and dihydroxyacetone, both of which are slowly attacked by yeast, whilst dihydroxyacetone is also fermented by yeast juice prepared by maceration (von Lebedev, Z. physiol. Chem. 1913, **84**, 305).

The Pyruvic Acid Theory of Fermentation.—The universal presence of carboxylase in yeasts capable of producing alcoholic fermentation creates a strong presumption that the decomposition of pyruvic acid actually forms a stage in the alcoholic fermentation of sugars. The fact that the evolution of carbon dioxide from pyruvic acid commences instantly, whereas there is a considerable delay in the case of glucose (Neuberg and Rosenthal, Biochem. Z. 1913, **51**, 128) is interpreted to mean that the glucose undergoes a preliminary change which requires some time and results in the formation of pyruvic acid capable of immediate decomposition. Other explanations of this delay, which is by no means invariable, can, however, be given. A number of observations have also been made by von Euler and his school which have led him to the same conclusion, that some intermediate product is formed before the production of alcohol and carbon dioxide.

Calcium pyruvate has actually been isolated by Fernbach and Schoen (Compt. rend. 1913, **157**, 1478; 1920, **170**, 764) from the products formed by the alcoholic fermentation of sugar by certain yeasts in the presence of chalk; but Kerb (Ber. 1919, **52** [B], 1795), using pure cultures of top and bottom fermentation yeasts, found no trace of pyruvate in the calcium salts formed (*cf.* Kerb and Zeckendorf, Biochem. Z. 1921, **122**, 307).

The pyruvic acid theory of alcoholic fermentation (Neubauer and Fromherz, Z. physiol. Chem. 1911, **70**, 326; Neuberg and Kerb, Z. Gärungsphysiol. 1912, **1**, 114; Kostytschev, Z. physiol. Chem. 1912, **79**, 130) involves three stages, exemplified by the following equations:

$$\text{(i)}\ C_6H_{12}O_6=2CH_3{\cdot}CO{\cdot}COOH+4[H];$$
$$\text{(ii)}\ 2CH_3{\cdot}CO{\cdot}COOH=2CH_3{\cdot}CHO+2CO_2;$$
$$\text{(iii)}\ 2CH_3{\cdot}CHO+4H=2CH_3{\cdot}CH_2{\cdot}OH.$$

The products of decomposition of pyruvic acid by yeast being carbon dioxide and acetaldehyde, the production of alcohol from glucose by way of pyruvic acid must involve a process of reduction. That yeast possesses powerful reducing properties has long been known (*philothion* of Rey-Pailhade). These are shared by yeast juice and the other active preparations obtained from yeast, all of which are capable of reducing many aldehydes to alcohols and various colouring matters to their leuco-compounds, and were therefore supposed to contain a reducing enzyme or *reductase*. These reactions are now recognised as belonging to the type of oxido-reductions effected by dehydrogenases. The intervention of this reducing enzyme of yeast in alcoholic fermentation was suggested by Grüss (Z. ges. Brauw. 1904, **27**, 689), and was supported by many workers, notably Palladin (Z. physiol. Chem. 1908, **56**, 81), Kostytschev (numerous papers in Z. physiol. Chem. from 1912), and Lvov (1913). The attempts made by these investigators to show that in presence of reducible substances the fermentation of glucose was modified (Lvov; Kostytschev), or that the presence of glucose interfered with the reduction of other substances, were not conclusive. Neuberg, however (in a series of papers summarised in Ber. 1919, **52** [B], 1677), has shown that in the presence of substances capable of combining with acetaldehyde the course of the fermentation is profoundly modified. For this purpose he employed normal sodium sulphite, which reacts with acetaldehyde according to the equation

$$C_2H_4O+Na_2SO_3+H_2O=C_2H_4O{\cdot}NaHSO_3+NaOH$$

In the presence of this salt, under the most favourable conditions, only about 30% of the sugar undergoes the normal fermentation, whilst the remaining 70% yields acetaldehyde, glycerol and carbon dioxide according to the equation $C_6H_{12}O_6=C_2H_4O+C_3H_8O_3+CO_2$, or, including the sulphite,

$$C_6H_{12}O_6+Na_2SO_3+H_2O=C_3H_8O_3+C_2H_4O{\cdot}NaHSO_3+NaHCO_3$$

The sulphite is best added after the fermentation has commenced, from 33 to 150 g. being used for 100 g. cane-sugar dissolved in 1–2·5 litres of water, and about 10–20 g. of yeast. Molecular proportions of acetaldehyde and glycerol are produced throughout the whole course of the fermentation, and the yield, referred to sugar, increases with the concentration of sulphite. Insoluble sulphites (**Ca, Zn, Mg**) can be used if the mixture is well agitated, and the process can also be carried out in faintly acid solution in the presence of acid potassium phosphate.

An enhanced production of acetaldehyde and glycerol had previously been observed by Neuberg and Färber (Biochem. Z. 1917, **78**, 238), both with living yeast and maceration juice in presence of a number of alkaline salts, but the acetaldehyde found was not chemically equivalent to the glycerol. It has now been found, however, that in these circumstances the acetaldehyde undergoes a Cannizzaro reaction, yielding alcohol and acetic acid, so that the fermentation in presence of alkalis proceeds as follows: $2C_6H_{12}O_6$

$$\longrightarrow 2C_3H_8O_3+2CO_2+2C_2H_4O \xrightarrow[+H_2O]{}$$

$$2C_3H_8O_3+2CO_2+C_2H_6O+C_2H_4O_2$$

One molecule of acetic acid is thus produced for every two molecules of glycerol. The yield of glycerol obtained in this way is not so high as in the presence of sulphite, amounting in the presence of sodium bicarbonate to about 35% of the theoretical (Neuberg and Hirsch, *ibid.* 1919, **100**, 304). Neuberg explained the results obtained, on the general lines of the pyruvic acid theory, by supposing that the sulphite combined with the acetaldehyde and thus prevented its reduction to alcohol, the glycerol being formed by the action of the hydrogen thus rendered available on the precursor of pyruvic acid, which he assumed to be methylglyoxal.

Wo. Ostwald (*ibid.* 1919, **100**, 279; *see also* Neuberg, *ibid.* 289) has pointed out that the enhanced production of acetaldehyde would naturally follow on the removal of this substance from the sphere of action, the equilibrium being in this way constantly disturbed, so that this fact cannot in itself be regarded as a strict proof of the theory that pyruvic acid is an intermediate product in the normal course of fermentation. In view of the fact that in the modified fermentation the acetaldehyde is produced at approximately the same rate as alcohol in the normal fermentation there can be little doubt that Neuberg's explanation is in this particular correct.

Technically the possibility of producing a large proportion of glycerol from sugar by fermentation in presence of sulphite has been made the basis of a process of manufacture of this substance (the Protol process), which has been worked on such a scale as to produce a million kg. of glycerol per month in a yield of 20–25% of the sugar employed (Connstein and Lüdecke, Ber. 1919, **52** [B], 1385).

An entirely different explanation of the origin of the glycerol in these fermentations is afforded by the newer theory of alcoholic fermentation (p. 30).

Phosphorylated Intermediate Compounds in the Alcoholic Fermentation of Sugar.

Since 1932 the participation of methylglyoxal in alcoholic fermentation has been rendered extremely improbable by the researches of Embden, Meyerhof and other workers (*see below*), according to which the sugar is first phosphorylated and then decomposed, the first phosphorus-free compound to be produced being pyruvic acid, the decomposition of which then proceeds as supposed by Neuberg. An important step in this direction was made when Meyerhof (Biochem. Z. 1927, **183**, 176) showed that when lactic acid was produced from glucose by muscle extract containing *hexokinase* (*see later*) the phenomena were closely analogous to those which occurred in alcoholic fermentation by yeast juice. In both cases a thermolabile enzyme system and a thermostable co-enzyme were required and yeast extract could supply the co-enzyme necessary for the muscle enzyme, and muscle extract that required for the yeast enzyme. Inorganic phosphate was rapidly esterified, the equation of Harden and Young held good and the rate of fermentation fell when all the inorganic phosphate had been esterified. Previous to this Embden and his colleagues had shown (*ibid.* 1915, **93**, 1, 124) that hexosediphosphate added to muscle press-juice caused an increase in the amounts of lactic and phosphoric acids formed, and later Embden and Zimmermann (Z. physiol. Chem. 1927, **167**, 114) isolated from muscle press-juice a hexosemonophosphoric ester (*lactacidogen*, or Embden ester) which they regarded as a precursor of the lactic acid. Since that time the development of our knowledge of alcoholic fermentation by yeast and of lactic acid formation by muscle has proceeded on parallel lines, the two subjects having been mutually helpful. The phenomena in muscle are only dealt with here in so far as they throw light on the subject of alcoholic fermentation. (For further information *see* Meyerhof, "Die chemischen Vorgänge im Muskel," Berlin, 1930, and Reviews by Robison, Ann. Rev. Biochem. 1936, **5**, 181; Parnas, Ergebn. Enzymforsch. 1937, **6**, 57; Meyerhof, Ergebn. Physiol. 1937, **39**, 10).

As early as 1930 Nilsson observed that when yeast was treated with acetaldehyde in presence of sodium fluoride, the aldehyde disappeared and at the same time an acid of the composition of phosphoglyceric acid was produced (Arkiv Kemi, Min., Geol. 1930, **10**, A, No. 7). At about the same time Lohmann (Biochem. Z. 1930, **222**, 324; Lipmann and Lohmann, *ibid.* 1930, **222**, 389) found that hexosediphosphate was converted (to the extent of 83%) by diluted muscle extract into an ester which could only be hydrolysed by acid with great difficulty. A similar substance was formed from glycogen and starch by muscle or its extract in presence of sodium fluoride and also from hexosediphosphate by muscle extract in presence of sodium fluoride. These compounds were at the time thought to be new forms of hexosediphosphate but were subsequently recognised as mixtures of phosphoric esters of glyceric acid and glycerol.

The next step was taken by Embden, Deuticke and Kraft (Klin. Woch. 1933, **12**, 213) who obtained phosphoglyceric acid from minced muscle in presence of certain salts (lactate, oxalate and fluoride of sodium) and came to the conclusion that Lohmann's new esters must also contain this compound.

They further made the fundamentally important observation that phosphoglyceric acid was decomposed by minced muscle into pyruvic acid ($CH_3{\cdot}CO{\cdot}COOH$) and free phosphoric acid. From a consideration of these facts they came to the conclusion that the hexosediphosphate underwent a primary fission into two molecules of phosphotriose (supposed by Embden to be 3-phosphoglyceraldehyde, $CH_2(O{\cdot}PO_3H_2){\cdot}CH(OH){\cdot}CHO$), and phospho-dihydroxyacetone,

$$CH_2(OH){\cdot}CO{\cdot}CH_2(O{\cdot}PO_3H_2)$$

which then underwent dismutation into a mixture of phosphoglyceric acid and phosphoglycerol:

1 mol. hexosediphosphate → 2 mol. phosphotriose → 1 mol. phosphoglyceric acid + 1 mol. phosphoglycerol

$$CH_2(O{\cdot}PO_3H_2){\cdot}CH(OH){\cdot}COOH$$
$$CH_2(O{\cdot}PO_3H_2){\cdot}CH(OH){\cdot}CH_2{\cdot}OH$$

They did not identify the phosphoglycerol, but showed that, although it was itself scarcely affected by minced muscle, when it was added to this along with phosphoglyceric acid, practically the whole of both compounds was converted into lactic acid and H_3PO_4. Embden assumed that in this reaction the pyruvic acid originating from the phosphoglyceric acid was reduced to lactic acid whilst the phosphoglycerol was at the same time oxidised to phosphotriose.

Pyruvic acid + phosphoglycerol → lactic acid + phosphotriose.

The latter again passed by dismutation into a mixture of phosphoglyceric acid and phosphoglycerol and so on until the whole was converted into lactic acid H_3PO_4.

1 mol. hexosediphosphate → 2 mol. phosphotriose → 1 mol. phosphoglyceric acid + 1 mol. phosphoglycerol → 2 mol. lactic acid + 2 mol. H_3PO_4.

The production of phosphoglycerol was definitely established almost simultaneously with Embden's publication by Meyerhof and Kiessling (Biochem. Z. 1933, **264**, 40) who had approached the subject from a different direction. It had been found that pyruvic acid could be isolated in large amount when the decomposition of carbohydrate by muscle extract was carried out in presence of sodium sulphite as a fixation reagent (Meyerhof and McEachern, *ibid.* 1933, **260**, 417). Search for the complementary reduced compound showed that it was phosphoglycerol.

After the untimely death of Prof. Embden (25.vii.1933) the further study of this branch of the subject was carried out mainly by Meyerhof and his colleagues, whose chief contributions are summarised below without any attempt, however, to record them in strictly chronological order.

The mechanisms of the changes involving phosphorylation or dephosphorylation and of the oxido-reductions which occur are discussed later on in connection with the function of the co-enzyme.

I. The Production of Phosphoglyceric Acid and Phosphoglycerol from Hexosediphosphate.—This fundamental change can readily be experimentally realised either in muscle extract, as mentioned above, or in yeast-maceration extract, in the presence of sodium fluoride (0·05*M*), the function of which is to inhibit the further change of the phosphoglyceric acid (Meyerhof and Kiessling, *ibid.* 1933, **267**, 40, 313), and thus to allow the products of the reaction to accumulate. Further analysis has shown that, as presumed by Embden, the reaction takes place in two stages:

(*a*) Decomposition of hexosediphosphate into two molecules of phosphotriose.
(*b*) Dismutation of the phosphotriose into a mixture of phosphoglyceric acid and phosphoglycerol.

Hexosediphosphate added either to dialysed muscle extract or to dialysed yeast-maceration extract is decomposed into two molecules of phosphotriose, an equilibrium being very rapidly attained (in a few seconds) (Meyerhof and Kiessling, *ibid.* 1933, **267**, 313; Meyerhof and Lohmann, *ibid.* 1934, **271**, 89).

1 mol. hexosediphosphate ⇌ 2 mol. phosphotriose.

The phosphotriose was now found to consist almost entirely of phosphodihydroxyacetone,

$$CH_2(O{\cdot}PO_3H_2){\cdot}CO{\cdot}CH_2{\cdot}OH$$

The nature of the change has been proved, (*a*) by enzymic conversion of both natural and synthetic (Kiessling, Ber. 1934, **67** [B], 869) phosphodihydroxyacetone into hexosediphosphate (Meyerhof and Lohmann, 1934, *l.c.*), and (*b*) by the preparation of phosphodihydroxyacetone from hexosediphosphate in presence of bisulphite as a fixative at 60°, so that almost complete conversion of the hexosediphosphate occurs and large quantities of phosphodihydroxyacetone can be obtained (Meyerhof and Lohmann, Biochem. Z. 1934, **273**, 413).

The enzyme concerned was termed by Meyerhof *zymohexase*, but is now known as *aldolase* (see p. 26); no dialysable co-enzyme is required for the reaction.

The decomposition of 1 mol. of hexosediphosphate into 1 mol. each of phosphoglyceraldehyde and phosphodihydroxyacetone was postulated by Embden and his colleagues as an intermediate stage in the production of phosphoglyceric acid.

It has been proved experimentally that the reaction takes place in this manner and that the preponderance of phosphodihydroxyacetone actually observed in the product is due to the presence of an enzyme (*phosphoglyceraldehyde mutase*) which accompanies zymohexase and so rapidly converts phosphoglyceraldehyde almost completely into phosphodihydroxyacetone that the phosphoglyceraldehyde cannot be isolated (Meyerhof and Kiessling, Biochem. Z. 1935, **279**, 40).

Starting with pure phosphoglyceraldehyde the change is so rapid that it is almost complete before any hexosediphosphate is produced by the zymohexase also present.

When hexosediphosphate is decomposed by zymohexase in the presence of phenylhydrazine as a fixative, the hydrazones

$$\mathrm{CH_2(O{\cdot}PO_3H_2){\cdot}CH(OH){\cdot}CH{:}N{\cdot}NHPh}$$

and

$$\mathrm{CH_2(O{\cdot}PO_3H_2){\cdot}C{:}N{\cdot}NHPh{\cdot}CH_2{\cdot}OH}$$

are formed so rapidly that the isomerisation of the phosphoglyceraldehyde is prevented. The mixed hydrazones can be decomposed by benzaldehyde, and the resulting mixture contains 50% of each of the two phosphotrioses (Meyerhof. Bull. Soc. Chim. biol. 1938, **20**, 1033, 1045; 1939, **21**, 965).

The reaction as it occurs in yeast and muscle preparations may therefore be formulated as follows: the reverse change of phosphodihydroxyacetone to phosphoglyceraldehyde takes place during the synthesis of hexosediphosphate from the phosphotrioses.

$$\begin{aligned}&\text{Hexosediphosphate} \rightleftharpoons \\ &\qquad \text{Phosphodihydroxyacetone} \\ &\qquad\qquad + \\ &\qquad \text{Phosphoglyceraldehyde} \rightleftharpoons \\ &\qquad\qquad \text{Phosphodihydroxyacetone}\end{aligned}$$

The two phosphotrioses are distinguishable chemically by their behaviour towards iodine in alkaline solution. Both the original substances are readily hydrolysed by *N*-alkali at room temperature, yielding lactic and phosphoric acids, and are hydrolysed by *N*-HCl at 100° to phosphoric acid and methylglyoxal. On treatment with iodine the phosphoglyceraldehyde is oxidised and the product is no longer hydrolysable by alkali in this way, whereas the phosphodihydroxyacetone is unaffected by iodine.

The enzymic equilibrium between hexosediphosphate and phosphodihydroxyacetone has been very thoroughly studied by Meyerhof and his colleagues (Meyerhof and Lohmann, Biochem. Z. 1934, **271**, 89; Meyerhof, *ibid.* 1935, **277**, 77). The equilibrium constant

$$K = \frac{[\text{Phosphodihydroxyacetone}]^2}{[\text{Hexosediphosphate}]}$$

varies greatly with the temperature, and has the values shown below.

Temp. °C.	$K \times 10^3$
−7	0·18
20	1·5
40	2·7
70	22

High temperature favours the conversion into the phosphotriose. At 20° the molecular proportions of the compounds are almost equal, 33% of the phosphorus being present as phosphotriose and 67% as hexosediphosphate.

By the use of the value of K for this equilibrium, the amount of hexosediphosphate present in an enzymic equilibrium mixture can be calculated from the amount of phosphate set free by alkaline hydrolysis in the cold (phosphodihydroxyacetone) (*cf.* Meyerhof and Kiessling, *ibid.* 1935, **283**, 89).

From the change of the value with the temperature the heat of reaction can be calculated from van't Hoff's equation

$$-Q = RT^2\frac{dlnK}{dT}$$

and is found to be −13,000 g.-cal. in good agreement with that actually measured (−14,000 g.-cal.) (Meyerhof and Lohmann, *ibid.* 1934, **273**, 73).

Meyerhof has further found (Meyerhof, Lohmann and Schuster, *ibid.* 1936, **286**, 301, 319) that the action of zymohexase in breaking or building up the carbon chain of hexosediphosphate is a particular instance of the action of an enzyme, termed by him *aldolase*, which specifically catalyses the condensation of phosphodihydroxyacetone with aldehydes, *e.g.*:

Phosphodihydroxyacetone + acetaldehyde ⇌ methyltetrosephosphate
Phosphodihydroxyacetone + glyceraldehyde ⇌ fructose-1-phosphate.

but has no effect on a mixture of phosphoglyceraldehyde and dihydroxyacetone, or of dihydroxyacetone and glyceraldehyde, etc.

Aldolase (zymohexase) occurs very widely in animal tissues and also in yeast, but is most concentrated in muscle, about 1/20 of this in yeast and still less in animal tissues other than muscle (Meyerhof and Lohmann, *ibid.* 1934, **273**, 413).

(*b*) *Dismutation of Phosphotriose into a Mixture of Phosphoglycerol and Phosphoglyceric Acid.*—This change, which is one of the fundamental reactions of Embden's scheme, can most easily be formulated on chemical grounds as proceeding by way of phosphoglyceraldehyde, and in view of Meyerhof's work, it seems probable that it actually occurs in this way.

$$\mathrm{2CH_2(O{\cdot}PO_3H_2){\cdot}CH(OH){\cdot}CHO + H_2O}$$

Phosphoglyceraldehyde.

$$\mathrm{= CH_2(O{\cdot}PO_3H_2){\cdot}CH(OH){\cdot}COOH}$$

Phosphoglyceric acid.

$$\mathrm{+ CH_2(O{\cdot}PO_3H_2){\cdot}CH(OH){\cdot}CH_2{\cdot}OH}$$

Phosphoglycerol.

The dismutation requires the presence of co-zymase. It is not affected by sodium fluoride, but is completely inhibited by 0·006 *M* iodoacetic acid (Meyerhof and Kiessling, *ibid.* 1933, **267**, 317).

The reaction occurs with either hexosediphosphate or phosphotriose in fluoride-containing yeast-maceration extract, or muscle extract. When synthetic *dl*-phosphoglyceraldehyde is used only the (+) component, which alone is fermentable by yeast (Smythe and Gerischer, *ibid.* 1933, **260**, 414), undergoes the change.

Experimentally stoichiometric equivalence is not as a rule strictly realised, phosphoglyceric acid usually preponderating to a greater or less extent over phosphoglycerol.

If acetaldehyde be added to the mixture, the aldehyde is reduced to alcohol and a corresponding equivalent of phosphotriose is oxidised to phosphoglyceric acid. In presence of both aldehyde and glucose (and inorganic phosphate) a considerable amount of esterification occurs and the amount of phosphoglyceric acid obtained may be greatly in excess of the phosphotriose or hexosediphosphate taken (*see later*).

II. Decomposition of Phosphoglyceric Acid.—It has been shown by Meyerhof that this decomposition is accomplished by way of a series of reactions involving (*a*) isomerisation of phosphoglyceric acid; (*b*) conversion of 2-phosphoglyceric acid into 2-phosphopyruvic acid; and (*c*) decomposition of phosphopyruvic acid.

(*a*) *Isomerisation of Phosphoglyceric Acid* (Meyerhof and Kiessling, *ibid.* 1935, **276**, 239).

The phosphoglyceric acid formed by the dismutation or oxidation of phosphotriose in muscle or yeast extract is a mixture of the two optically active isomers, 3-phosphoglyceric acid $[\alpha]_D$ −14·5° and 2-phosphoglyceric acid, $[\alpha]_D$ +24·3°.

The acid barium salt of the 2-acid is more readily soluble than that of the 3-acid, so that they can be separated and isolated from the mixed product obtained by the action of fluoride-containing extract of yeast or muscle on hexosediphosphate, acetaldehyde and glucose.

When the salts of the pure isomers are added to dialysed muscle extract (containing fluoride to prevent the formation of phosphopyruvic acid), an equilibrium is very rapidly set up, a specific enzyme, ***phosphoglyceromutase***, being present in the extract.

3-Phosphoglyceric acid$\rightleftharpoons$2-Phosphoglyceric acid

Temp. °C.	K	3-phospho-glyceric acid. %	2-phospho-glyceric acid. %
20	4·7	82·5	17·5
28	3·85	79·3	20·7
60	2·3	70	30

The equilibrium is very sensitive to temperature as shown by the change in K as given above.

The same equilibrium is set up when the synthetic *dl*-phosphoglyceric acids (Kiessling, Ber. 1935, **68** [B], 143) are used, but in this case the equilibrium is between the naturally occurring isomers, the *l*-isomers being unaffected. This observation has led to a new type of biological resolution of a *dl*-mixture (Meyerhof and Kiessling, Biochem. Z. 1935, **276**, 239).

(*b*) *Conversion of 2-Phosphoglyceric Acid into Phospho-(enol)-pyruvic Acid.*—When a phosphoglycerate is added to dialysed or inactivated muscle extract or to dialysed yeast-maceration extract, in addition to the equilibrium between 3- and 2-phosphoglyceric acids a second equilibrium is set up between 2-phosphoglyceric acid (30%) and phospho-(enol)-pyruvic acid (70%) (Lohmann and Meyerhof, Biochem. Z. 1934, **273**, 60).

Phosphopyruvic acid can be separated from the phosphoglyceric acids by means of its more soluble **Ba** salt, and it forms a crystalline **AgBa** salt. The synthetic acid, prepared by Kiessling (Ber. 1935, **68** [B], 597) by the action of $POCl_3$ on pyruvic acid dissolved in quinoline, has the same properties as the acid isolated from muscle extract. It is completely hydrolysed to pyruvic and phosphoric acids by *N*-HCl at 100° in 10 minutes. $HgCl_2$ added to its aqueous solution decomposes it very rapidly into phosphoric and pyruvic acids. It takes up 6 atoms of iodine in alkaline solution, as does pyruvic acid, forming iodoform and phosphoric acid. It probably has the constitution

$$CH_2{:}C(O{\cdot}PO_3H_2){\cdot}COOH$$

The equilibrium between 2-phosphoglyceric acid and phosphopyruvic acid is complicated by the fact that in muscle and yeast extracts the isomeric 3- and 2-phosphoglyceric acids also exist in enzymic equilibrium. However, the enzyme (*enolase*) which catalyses the phosphopyruvic equilibrium can be obtained by adsorption on charcoal almost free from the phosphoglyceromutase (Akano, Biochem. Z. 1935, **280**, 110), so that starting with phosphopyruvic acid practically no formation of 3-phosphoglyceric acid occurs. In these circumstances the equilibrium between 2-phosphoglyceric acid and phosphopyruvic acid is found to be almost independent of temperature (in contrast to that between the isomeric phosphoglyceric acids). The constant K=2·3 so that in equilibrium 70% of phosphopyruvic acid and 30% of 2-phosphoglyceric acid are present.

Where both enzymes are present, as in dialysed muscle or yeast extract, the final equilibrium depends on the temperature. At 28° the equilibrium mixture contains 3-phosphoglyceric acid 55·2%, 2-phosphoglyceric acid 13·8%, phosphopyruvic acid 31%.

Starting with 2-phosphoglyceric acid there is usually a rapid formation of phosphopyruvic acid, and the amount of this then gradually diminishes as the conversion of 2-phosphoglyceric acid into the 3-isomeride proceeds.

The reaction is completely inhibited by sodium fluoride but not by iodoacetic acid. It does not require a dialysable co-enzyme.

(*c*) *Decomposition of Phosphopyruvic Acid.*—Both phosphoglyceric and phosphopyruvic acids are readily decomposed by muscle extract yielding pyruvic acid and phosphoric acid,

$$CH_2{:}C(O{\cdot}PO_3H_2){\cdot}COOH+H_2O$$
$$=H_3PO_4+CH_3{\cdot}CO{\cdot}COOH$$

provided that the co-enzyme system consisting of adenylic acid and **Mg** is present, and this reaction forms an essential part of the schemes of fermentation of Embden and Meyerhof. The fate of the phosphoric acid and the mechanism of dephosphorylation are discussed later on.

In untreated yeast-maceration extract, containing the co-enzyme system, the same change occurs, but the pyruvic acid is further decomposed into acetaldehyde and CO_2. This decomposition of phosphopyruvic acid is not affected either by iodoacetic acid or sodium fluoride, whereas as mentioned above, the conversion of phosphoglyceric into phosphopyruvic acid is completely inhibited by sodium fluoride.

III. Reduction of Pyruvic Acid in Muscle Extract and of Acetaldehyde in Yeast Preparations. I. *Lactic Acid Formation in Muscle Extract.*—It was found by Embden (1933) that the reduction of pyruvic acid to lactic acid in muscle pulp was due to reaction with phosphoglycerol, a phosphotriose being probably formed intermediately.

Abundant confirmation that this reaction can occur was supplied by the experiments of Meyerhof and Kiessling, who in 1933, following Embden, summed up the changes, commencing with phosphoglyceric acid, as follows (*ibid.* 1933, **264**, 40).

Phosphoglyceric acid → Pyruvic acid + H_3PO_4
Pyruvic acid + Phosphoglycerol
→ 2 mol. Lactic acid + H_3PO_4

Both these changes require the presence of a co-ferment system. These reactions will be further discussed on p. 34.

2. *Alcohol Formation in Yeast Extract.*—In alcoholic fermentation the changes appear to be identical with those just described for lactic acid production as far as the production of pyruvic acid. In yeast preparations this is decomposed by the carboxylase into acetaldehyde + CO_2.

The aldehyde is then reduced by interaction with phosphotriose (Meyerhof and Kiessling, *ibid.* 1933, **267**, 313) which is simultaneously oxidised to phosphoglyceric acid.

Phosphotriose + acetaldehyde + H_2O
→ Phosphoglyceric acid + alcohol.

This reaction is inhibited by iodoacetic acid but not by fluoride. Its mechanism is discussed later (p. 32). In the rapid production of lactic acid from glucose in muscle extract in presence of phosphate (and hexokinase), however, pyruvic acid reacts with phosphotriose, not phosphoglycerol, lactic acid and phosphoglyceric acid being produced (along with an equivalent amount of hexosediphosphate), as in the analogous change in alcoholic fermentation (p. 31). Pyruvic acid can also react with hexosediphosphate (by way of phosphotriose) in presence of NaF, lactic acid and phosphoglyceric acid being formed.

IV. Equations of Alcoholic Fermentation by Yeast Preparations.—The reactions just discussed can be expressed in a simple series of equations which give a quantitative account of the decomposition of hexosediphosphate alone, or in presence of glucose, by yeast preparations:

1. Hexosediphosphate ⇌ 2 Phosphotriose.
2. 2 Phosphotriose + 2 Acetaldehyde → 2 Phosphoglyceric acid + 2 Alcohol.
3. 2 Phosphoglyceric acid → 2 Pyruvic acid + $2H_3PO_4$.
4. 2 Pyruvic acid → $2CO_2$ + 2 Acetaldehyde.

In presence of glucose the H_3PO_4 of equation 3 is not liberated in the free state but is transferred to glucose, ultimately forming hexosediphosphate, which is then decomposed as in equation 1, and this series of changes usually continues until all the glucose has been fermented. If the amount of co-zymase present becomes insufficient for the fermentation of glucose whilst sufficient is present for the fermentation of hexosediphosphate (p. 19), inorganic phosphate may accumulate even in presence of glucose.

All these reactions proceed very slowly compared with the rate of fermentation of glucose in presence of phosphate, and this is in agreement with the observed fact that the fermentation of hexosediphosphate is a relatively slow process (Meyerhof and Kiessling, *ibid.* 1935, **281**, 249), its rate of fermentation being only 3–5% and those of phosphoglyceric and phosphopyruvic acids only 10–15 and 15–20% respectively of that of glucose in the presence of phosphate.

Further progress was made by Meyerhof and Kiessling (*ibid.* 1935, **281**, 249), who observed that when the fermentation of phosphopyruvic acid was carried out in the presence of glucose and phosphate, the reaction was modified:

(*a*) The rate of fermentation was greatly increased and became equal to or greater than that of glucose in the presence of phosphate.
(*b*) The phosphoric group of the phosphopyruvic acid appeared to be transferred to glucose forming hexosediphosphate.
(*c*) A second molecule of glucose became esterified at the expense of the inorganic phosphate and was decomposed into CO_2 and alcohol.

The mechanism of the reaction was discovered by carrying out the fermentation in presence of NaF. Under these conditions the second molecule of glucose was converted into phosphoglyceric acid and not further changed.

The reaction under these conditions, *i.e.* in presence of NaF, may therefore be expressed by the two equations:

(5*a*) 2 mol. Phosphopyruvic acid + 1 mol. Glucose → 1 mol. Hexosediphosphate + $2CO_2$ + 2 mol. Acetaldehyde;
(5*b*) 1 mol. Glucose + 2 mol. Acetaldehyde + $2H_3PO_4$ → 1 mol. Hexosediphosphate + 2 mol. Acetaldehyde ⇌ 2 mol. Phosphotriose + 2 mol. Acetaldehyde → 2 mol. Phosphoglyceric acid + 2 mol. Alcohol;

or summarised:

(5) 2 mol. Phosphopyruvic acid + 2 mol. Glucose + $2H_3PO_4$ → $2CO_2$ + 2 mol. Alcohol + 2 mol. Phosphoglyceric acid + 1 mol. Hexosediphosphate.

In presence of iodoacetic acid which completely inhibits the oxido-reduction of phosphotriose and acetaldehyde but does not inhibit the decomposition of either phosphoglyceric acid or phosphopyruvic acid, the reaction also proceeds at the high rate, but takes the form

2 mol. Phosphopyruvic acid + 1 mol. Glucose
→ $2CO_2$ + 2 mol. Acetaldehyde + 1 mol. Hexosediphosphate.

The essential point seems to be the phosphorylation of the extra molecule of sugar, and it is only when this occurs that the high rate of reaction is attained. Experiments with different sugars and their derivatives show that the rates of fermentation of phosphopyruvic acid in presence of NaF and of phosphoglyceric and phosphopyruvic acids in presence of iodoacetic acid are intimately bound up with the rate of esterification and fermentation of the added substance. Thus fructose, glucose and mannose all give a large increase, hexosemonophosphate a lower one, glycogen a still lower one; galactose gives a very low increase, dihydroxyacetone and glyceraldehyde a still lower one, and mannitol which is non-fermentable only a trace of increase over phosphopyruvic acid alone. These increases correspond with the rates of fermentation of the added substances in the absence of inhibitants.

These results were embodied by Meyerhof and Kiessling (*ibid.* 1935, **281**, 249) in a new scheme of fermentation which has now been modified as the result of a further analysis of the individual reactions. This has been rendered possible by the use of a restricted system of enzymes in which not only were pure co-enzymes used but the apo-enzymes were also partially purified. Warburg and Christian devised a fermentation system of this kind (*ibid.* 1936, **287**, 291) for testing the efficacy of co-zymase (Co-dehydrogenase I).

To a solution containing hexosemonophosphate (Robison fermentation ester), inorganic phosphate and acetaldehyde the following additions are made:

(*a*) Two "specific proteins" (apo-enyzmes), A and B, prepared by Negelein (*ibid.* 1936, **287**, 329) from yeast-maceration extract by precipitation first with acetic acid (A) and then with acetone (B).

(*b*) Adenylpyrophosphate and co-dehydrogenase I.

(*c*) **Mg** ions (**Mn** ions are possibly also necessary; NH_4 ions are present in the yeast preparation A).

A coupled reaction then occurs, which was interpreted in the following way (a different interpretation is given by Meyerhof and his colleagues, p. 30):

1. Hexosemonophosphate + 2 Acetaldehyde + H_2O → Pyruvic acid + Phosphoglyceric acid + 2 Alcohol;
2. Hexosemonophosphate + H_3PO_4 → Hexosediphosphate + H_2O;

or summarised:

3. 2 Hexosemonophosphate + 2 Acetaldehyde + 1 Phosphoric acid → 1 Hexosediphosphate + 1 Pyruvic acid + 1 Phosphoglyceric acid + 2 Alcohol.

Carboxylase is absent, so that the pyruvic acid is not further changed.

A further study of this system has been made by Meyerhof, Kiessling and Schulz (*ibid.* 1937, **292**, 25). Although glucose is not attacked under these conditions and hexosediphosphate only very slowly, a mixture of the two is fermented even more rapidly than hexosemonophosphate itself.

Function of "Proteins" A and B.—It has been found that protein A is essential for the reaction by which hexosediphosphate is formed by transference of phosphate from phosphopyruvic acid to glucose or hexosemonophosphate (by way of adenylpyrophosphate (*see later*, p.34)). Every formation of hexosediphosphate requires the presence of protein A. Protein B on the other hand contains the apo-enzymes for the dehydrogenase, necessary for the production of hexosemonophosphate from inorganic phosphate, by way of adenylpyrophosphate, since this reaction is coupled with oxido-reduction, and for the various enzymes concerned in the production of phosphopyruvic acid from hexosediphosphate. *When protein A is omitted* from Warburg and Christian's system, no change occurs, as the hexosemonophosphate cannot be converted into the diphosphate which is a necessary preliminary to its decomposition. When, however, protein A is omitted from the modified system containing glucose and hexosediphosphate, the following reaction occurs, the hexosediphosphate and phosphoglyceric acid being respectively in equilibrium with phosphotriose and phosphopyruvic acid:

(*a*) Hexosediphosphate (⇌Phosphotriose) + 2 Glucose + $2H_3PO_4$ + 2 Acetaldehyde = 2 Phosphoglyceric acid (⇌Phosphopyruvic acid) + 2 Hexosemonophosphate + 2 Alcohol.

This shows that the origin of the phosphoglyceric acid in this reaction (and of the pyruvic acid formed from it in reaction (*b*) (*below*)) is the hexosediphosphate and not the glucose. **NaF** makes no difference except that it inhibits the equilibrium between phosphoglyceric acid and phosphopyruvic acid. If *protein A be now added*, a further reaction occurs:

(*b*) 2 Phosphoglyceric acid (⇌Phosphopyruvic acid) + 2 Hexosemonophosphate = 2 Pyruvic acid + 2 Hexosediphosphate.

The sum of these two reactions (*a*+*b*) represents the rapid fermentation in presence of glucose and hexosediphosphate in the restricted system.

(*a* + *b*) Hexosediphosphate + 2 Glucose + $2H_3PO$ + 2 Acetaldehyde = 2 Alcohol + 2 Pyruvic acid + 2 Hexosediphosphate.

In the unrestricted system, the pyruvic acid is decomposed and the summarised equation becomes:

(*c*) Hexosediphosphate + 2 Glucose + $2H_3PO_4$ = $2CO_2$ + 2 Alcohol + 2 Hexosediphosphate.

These observations are borne out by many others on the effects of varying the nature and quantity of the substrates present and have been embodied by Meyerhof in his latest scheme of fermentation (Meyerhof, Kiessling and Schulz, *ibid.* 1937, **292**, 25, 65; *see also* Meyerhof, Ergebn. Physiol. 1937, **39**, 10).

The main features of the scheme (p. 30) are the following:

1. The substance broken down to 3-carbon compounds is always hexosediphosphate. The breakdown occurs in the way already described by way of phosphotriose, etc. This follows directly from the experiments with the restricted fermentation system. Further proof is afforded by the fact that when the glucose of the modified fermentation test is replaced by creatine (+dialysed muscle extract) the formation of pyruvic acid, the only possible source of which is the hexosediphosphate, proceeds at the usual high rate. The creatine not only accepts the phosphate from the phosphopyruvic acid formed intermediately, but also takes up an equal quantity of inorganic phosphate, this reaction

Meyerhof's Scheme II of the Stationary Phase (B) (*Reaction of 2 mol. glucose*).

α 1 M. hexosediphosphate $\rightleftharpoons$ 1 M. phosphoglyceraldehyde + 1 M. phosphodihydroxyacetone $\rightleftharpoons$ 1 M. phosphodihydroxyacetone } = 2 M. phosphotriose

η 2 M. phosphotriose + 2 M. *glucose* + 2 M. *phosphoric acid* + 2 M. acetaldehyde $\leftarrow$

= 2 M. 3-phosphoglyceric acid + 2 M. hexosemonophosphate + 2 M. alcohol

δ 2 M. 3-phosphoglyceric acid. $\rightleftharpoons$ 2 M. 2-phosphoglyceric acid $\rightleftharpoons$ 2 M. phosphopyruvic acid + $2H_2O$

θ 2 M. hexosemonophosphate + 2 M. phosphopyruvic acid = 2 M. pyruvic acid + 2 M. hexosediphosphate

ζ 2 M. pyruvic acid = $2CO_2$ + 2 M. acetaldehyde

being coupled with the oxido-reduction. Four mol. of phosphocreatine are thus produced.

2. The oxido-reduction of 2 mol. of phosphotriose and acetaldehyde, yielding phosphoglyceric acid and alcohol, is accompanied in presence of glucose and inorganic phosphate by the phosphorylation of 2 mol. of glucose by inorganic phosphate to form hexosemonophosphate. This requires co-zymase (co-phosphorylase and co-dehydrogenase) and protein B and is catalysed by hexosediphosphate. Hexosemonophosphate is thus the primary product of esterification of glucose. Further evidence in support of this conclusion is given in the section on Phosphorylation (p. 37).

3. The hexosemonophosphate is converted into hexosediphosphate by transference of phosphate from phosphopyruvic acid. (This requires protein A, Mg(Mn) and adenylic acid or other co-phosphorylase (*see later*, p. 34).)

4. In agreement with Harden and Young's original equation, the products formed from 2 mol. of glucose are 2 mol. each of CO_2 and alcohol + 1 mol. hexosediphosphate. The scheme shows that it is in the coupled reaction (η), in which 2 mol. phosphotriose are oxidised to form 2 mol. phosphoglyceric acid, that 2 mol. of inorganic phosphate are esterified to form 2 mol. hexosemonophosphate. These 2 mol of hexosemonophosphate are subsequently further esterified to hexosediphosphate by transference of the phosphate of the 2 mol. of phosphopyruvic acid resulting from the same coupled reaction. The CO_2 (2 mol.) arising from the decomposition of the pyruvic acid thus formed is accordingly equivalent to the inorganic phosphoric acid (2 mol.) which has been esterified.

It is not yet fully understood why the oxidation of 2 mol. of phosphotriose should be coupled with the esterification of precisely 2 mol. of H_3PO_4 rather than with less or more (*cf.* Needham and Pillai, Biochem. J. 1937, **31**, 1837), but the reason is probably to be sought in the energy relations of the two changes. It has been stated that in the fermentation of glycogen this relation does not hold, more phosphoric acid being esterified than corresponds with the CO_2 evolved (p. 37).

Meyerhof (Biochem. Z. 1937, **292**, 25) suggests that the presence of hexosemonophosphate in the products along with hexosediphosphate without disturbance of the ratio CO_2/esterified phosphoric acid (*see* p. 19) may be explained by the transference of the phosphoric acid of some of the phosphopyruvic acid directly to glucose, a corresponding amount of hexosemonophosphate being left unchanged.

Fermentation of Hexosemonophosphate.—The experiments of Meyerhof, Kiessling and Schulz (*ibid.* 1937, **292**, 25) with Warburg and Christian's restricted system (p. 29) have shown that in the main path of the alcoholic fermentation of glucose hexosemonophosphate is produced by the phosphorylation of glucose by inorganic phosphate (by way of adenylpyrophosphate). It is then converted into hexosediphosphate before being broken down to phosphotriose. This takes place by transfer of phosphate from phosphopyruvic acid. In Warburg and Christian's original test hexosemonophosphate undergoes two reactions, the first of which is catalysed by hexosediphosphate and the second of which requires protein A.

(1) 1 Hexosediphosphate ($\rightleftharpoons$2 phosphotriose) + 1 Hexosemonophosphate + 2 Acetaldehyde + H_3PO_4 $\rightarrow$ 2 Phosphoglyceric acid + 2 Alcohol + 1 Hexosediphosphate.

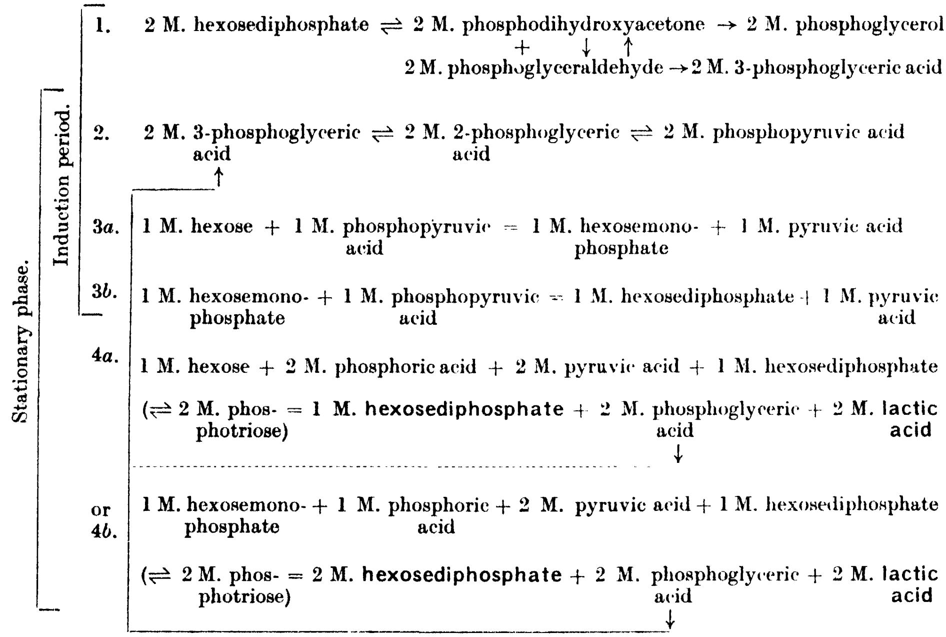
(2) 1 Hexosemonophosphate + 1 Phosphoglyceric acid $\rightarrow$ 1 Hexosediphosphate + 1 Pyruvic acid.

The hexosediphosphate in (1) appears to remain unaltered but in fact acts catalytically, being broken down and oxidised to phosphoglyceric acid, whilst a fresh quantity is formed by the phosphorylation of hexosemonophosphate. In the presence of NaF more monophosphate is phosphorylated and hence hexosediphosphate accumulates. When hexosemonophosphate is acted on by unrestricted yeast preparations, a rapid reaction ensues if inorganic phosphate is present, part of the monophosphate being fermented to CO_2 and alcohol and part converted into hexosediphosphate (Harden and Robison in " Alcoholic Fermentation " (Harden), 1932, p. 139; Meyerhof and Lohmann, Biochem. Z. 1927, **185**, 113; Meyerhof, *ibid.* 1934, **273**, 80; *cf.* von Euler and Myrbäck, Annalen, 1928, **464**, 56). The change has not been very thoroughly investigated, but it appears closely to correspond in principle with reactions 1 and 2 above. An analogous change is produced by muscle extract.

In all cases, according to Meyerhof, hexosemonophosphate is fermented by way of hexosediphosphate and phosphotriose.

THE MAIN PATH OF LACTIC ACID FORMATION IN MUSCLE EXTRACT.—Many of the reactions which are involved in the production of lactic acid in muscle extract have been incidentally discussed in the foregoing pages. Meyerhof sums them up in the following scheme (Ergebn. Physiol. 1937, **39**, 69) which applies strictly to the changes undergone by hexoses, in the absence of creatine, in muscle extract to which hexokinase has been added.

Modified Scheme for the Main Path of Lactic Acid Formation.


Stationary phase.
Induction period.

1. 2 M. hexosediphosphate $\rightleftharpoons$ 2 M. phosphodihydroxyacetone $\rightarrow$ 2 M. phosphoglycerol
+ $\downarrow$ $\uparrow$
2 M. phosphoglyceraldehyde $\rightarrow$ 2 M. 3-phosphoglyceric acid

2. 2 M. 3-phosphoglyceric acid $\rightleftharpoons$ 2 M. 2-phosphoglyceric acid $\rightleftharpoons$ 2 M. phosphopyruvic acid
$\uparrow$

3*a*. 1 M. hexose + 1 M. phosphopyruvic acid = 1 M. hexosemonophosphate + 1 M. pyruvic acid

3*b*. 1 M. hexosemonophosphate + 1 M. phosphopyruvic acid = 1 M. hexosediphosphate + 1 M. pyruvic acid

4*a*. 1 M. hexose + 2 M. phosphoric acid + 2 M. pyruvic acid + 1 M. hexosediphosphate
($\rightleftharpoons$ 2 M. phosphotriose) = 1 M. hexosediphosphate + 2 M. phosphoglyceric acid + 2 M. lactic acid
$\downarrow$

or 4*b*. 1 M. hexosemonophosphate + 1 M. phosphoric acid + 2 M. pyruvic acid + 1 M. hexosediphosphate
($\rightleftharpoons$ 2 M. phosphotriose) = 2 M. hexosediphosphate + 2 M. phosphoglyceric acid + 2 M. lactic acid
$\downarrow$

Creatine, as already explained, acts in presence of the adenylic acid system as a phosphate acceptor, and as such it can replace the hexose in reaction 4*a*. (For a detailed discussion of lactic acid formation in muscle, *see* Parnas, Ergebn. Enzymforsch. 1937, **6**, 57.)

Initial Phase of the Fermentation.—Before reactions η, δ, θ, ζ (p. 30) can take place at the maximum rate, there must be a sufficient supply both of phosphotriose, derived from hexosediphosphate, and acetaldehyde. As these are produced at a late stage of the reaction in the stationary phase (equations θ and ζ) there is an initial phase during which the supply of these substances and the rate of fermentation gradually increase.

Phosphoglyceric acid, from which the acetaldehyde is derived (equations δ, θ and ζ), is formed from phosphotriose by dismutation and the dismutation is accompanied by the esterification of a molecule of glucose first to hexosemonophosphate and then to hexosediphosphate. This reaction was formulated by Meyerhof and Kiessling (Biochem. Z. 1933, **267**, 313) and embodied in their first scheme of fermentation (*ibid.* 1935, **281**, 249) as follows:

A. Glucose + hexosediphosphate + $2H_3PO_4$ $\rightarrow$ [4 phosphodihydroxyacetone $\rightarrow$ 4 phosphoglyceraldehyde] $\rightarrow$ 2 α-phosphoglycerol + 2 phosphoglyceric acid.

It has now been further analysed into reactions α, β and γ of Meyerhof's Scheme II for the initial phase of the fermentation (*see* Meyerhof, Ergebn. Physiol. 1937, **39**, 65).

The phosphoglyceric acid is then decomposed according to reactions δ and ϵ (p. 32).

The phosphoglycerol simultaneously produced takes no further part in the reaction, but is rapidly hydrolysed by the *glycerophosphatase* present and is the source of the glycerol which was first observed among the products of fermentation by Pasteur.

These reactions (α, β, γ) continue until sufficient acetaldehyde and phosphotriose are being produced for the reactions of the stationary phase to proceed at the maximum rate. As soon

Meyerhof's Scheme II of the Initial Phase (A) (Reaction of 2 mol. glucose).

α 2 M. hexosediphosphate $\rightleftharpoons$ 2 M. phosphoglyceraldehyde $\rightleftharpoons$ 2 M. phosphodihydroxyacetone
+
2. M. phosphodihydroxyacetone.
} 4 M. phosphotriose

β 1 M. phosphoric acid + 1 M. *glucose* + 2 M. phosphotriose
= 1 M. hexosemonophosphate + 1 M. phosphoglycerol + 1 M. *phosphoglyceric acid*

γ 1 M. phosphoric acid + 1 M. hexosemonophosphate + 2 M. phosphotriose
= 1 M. hexosediphosphate + 1 M. phosphoglycerol + 1 M. *phosphoglyceric acid*

δ 2 M. 3-phosphoglyceric acid $\rightleftharpoons$ 2 M. 2-phosphoglyceric acid $\rightleftharpoons$ 2 M. phosphopyruvic acid + $2H_2O$

ε 2 M. phosphopyruvic acid + 1 M. glucose $\rightarrow$ 1 M. hexosediphosphate + 2 M. pyruvic acid
$\downarrow$
$2CO_2$ + 2 M. acetaldehyde

as this is the case, the fermentation passes completely into the stationary phase and the further changes appear to be effected entirely by reactions α, η, δ, θ, ζ. Phosphoglycerol ceases to be produced, whilst the hexosediphosphate (which is mixed with monophosphates) accumulates as shown in equation θ.

Period of Induction.—During the initial phase, the velocity of fermentation gradually increases, sometimes very slowly, until the rate corresponding with the stationary phase is reached. A prolonged period of induction is frequently observed with maceration extract (von Lebedev, Ann. Inst. Pasteur, 1912, **26**, 8) and with zymin or dried yeast suspended in a large volume of sugar solution (*see* Harden, "Alcoholic Fermentation," 1911, p. 40). This period is abolished by the presence of very small amounts (0·2 millimolecules) of hexosediphosphate (Meyerhof, Z. physiol. Chem. 1918, **102**, 185), of substances which readily lead to its formation, such as adenylpyrophosphate (*see* Ohlmeyer, Biochem. Z. 1936, **287**, 225), or of the intermediate products of its decomposition, phosphoglyceric acid (Lipmann, *ibid.* 1934, **274**, 412) and phosphopyruvic acid (Meyerhof and Kiessling, *ibid.* 1935, **280**, 99). Hence no prolonged induction period is observed with yeast juice in which, in contrast to what happens in maceration extract, these substances are produced by the autofermentation which is always going on. (*See also* on this subject Harden and Macfarlane, Biochem. J. 1928, **22**, 786; Katagiri and Yamagashi. *ibid.* 1929, **23**, 654; Patterson, *ibid.* 1931, **25**, 1593; Raymond and Levene, J. Biol. Chem. 1928, **79**, 621; Mayer, Biochem. Z. 1927, **186**, 313; Nilsson, Arkiv Kemi, Min., Geol. 1930, **10**, A, No. 7).

The period of gradual rise in the velocity of fermentation (Gäranstieg) which occurs when a phosphate is added to yeast preparations and sugar is one in which a similar increase of the rate of production of phosphotriose and acetaldehyde occurs. Its duration is greatly diminished in the presence of acetaldehyde and other reducible substances (Harden and Henley, Biochem. J. 1920, **14**, 642; 1921, **15**, 175) which act, as suggested by Neuberg, as hydrogen acceptors. This is probably the explanation of the stimulating effect on fermentation of many reducible substances which has been observed by Neuberg and his colleagues (Biochem. Z. 1918, **88**, 145; 1920, **101**, 239, 276; **109**, 290; 1921, **120**, 215).

Oxido-Reduction and Phosphorylation

In the foregoing scheme no reference is made to the mechanisms of the reactions. Two of the processes involved have received much attention; (*a*) the transfer of hydrogen in the oxido-reductions which occur; (*b*) the introduction of phosphoric groups into the sugar molecule.

FUNCTION OF CO-ZYMASE (CO-DEHYDROGENASE I; *Co*) IN THE REDUCTION OF ACETALDEHYDE AND OXIDATION OF PHOSPHOTRIOSE. 1. *The Reversible Action of Alcohol Dehydrogenase.*—It can readily be demonstrated by the use of purified co-zymase that the reaction between it and alcohol only occurs in presence of a specific apo-dehydrogenase (prepared from yeast) and is reversible, the equilibrium being far to the left of the equation given below.

$$Co + \text{alcohol} \rightleftharpoons CoH_2 + \text{acetaldehyde}$$

Acetaldehyde in presence of CoH_2 will therefore be almost completely reduced to alcohol, and it is this reaction which is responsible for the production of alcohol in alcoholic fermentation.

The change in the CoH_2 can be followed experimentally by measurement of the extinction coefficient (von Euler, Adler and Hellström, Z. physiol. Chem. 1936, **241**, 239; Warburg and Christian, Biochem. Z. 1936, **286**, 81; **287**, 291). This reaction can also be demonstrated visually because the CoH_2 fluoresces brilliantly in ultra-violet radiation. The addition of alcohol to a solution containing co-dehydrogenase I and its apo-dehydrogenase and exposed to ultra-violet rays (340 $m\mu$) is followed by fluorescence of the solution. Subsequent addition of acetaldehyde removes the 2 atoms of hydrogen from almost the whole of the $Co\mathrm{H}_2$ and the fluorescence ceases, provided that the apo-dehydrogenase is still present, but not if it has been inactivated by heat.

The constant of equilibrium is independent of the concentration of the enzyme but varies greatly with the p_{H} ($\mathrm{K}=7{\cdot}8\times10^{-4}$ at p_{H} 6·4; $0{\cdot}8\times10^{-4}$ at p_{H} 7·7). This is because the rate of dehydrogenation of alcohol is at its maximum at p_{H} 8 whereas the rate of hydrogenation of acetaldehyde is at its maximum at p_{H} 6–6·4.

2. *Phosphotriose Dehydrogenase.*—The function of co-zymase in the dehydrogenation of phosphotriose and in the dismutation of this substance to phosphoglyceric acid and phosphoglycerol has not been so thoroughly studied as its function in the alcohol–acetaldehyde reaction because the specific apo-dehydrogenase is difficult to obtain free from other apo-enzymes. It has, however, been investigated by experiments in which the hydrogen taken up by the *Co* from the substrate is transferred from the resulting $Co\mathrm{H}_2$ to Methylene Blue. This does not occur directly, but probably in the main by way of the enzyme *diaphorase* (von Euler, *see* p. 34*b*) and only to a smaller extent by way of Warburg's *flavin enzyme.* These enzymes have the property of taking up $2\mathrm{H}$ from the $Co\mathrm{H}_2$ and transferring it to the Methylene Blue, which is thereby decolorised. It has thus been found (von Euler and Adler, Arkiv Kemi. Min., Geol. 1936, **12**, B, No. 16) that in a mixture containing apo-dehydrogenase (alcohol precipitate from yeast maceration extract; von Euler and Adler, Z. physiol. Chem. 1934, **226**, 195, 205), co-zymase, diaphorase, phosphate buffer of p_{H} 7·6 and Methylene Blue, rapid decoloration occurs when phosphoglyceraldehyde is added, but only when co-zymase and diaphorase (or flavin enzyme) are present.

Dismutation of Phosphotriose to Phosphoglyceric Acid and Phosphoglycerol (*Glycerophosphoric Acid*).—As already explained (p. 31*b*), this change is only of importance in the processes of alcoholic fermentation and lactic acid production in the initial stage and is replaced by the oxido-reduction of phosphotriose and acetaldehyde (or pyruvic acid) as soon as sufficient of these compounds is being produced for the establishment of the stationary phase in which acetaldehyde (or pyruvic acid) acts as a hydrogen acceptor. The reaction may be formulated as follows (Adler and Hughes, *ibid.* 1938, **253**, 71), the transfer of hydrogen being effected as in the case of the alcohol dehydrogenation by way of the reversible change $Co \rightleftharpoons Co\mathrm{H}_2$.

(*a*) Phosphotriose (phosphoglyceraldehyde) + *Co*-phosphotriose - apo-dehydrogenase $\rightleftharpoons$ Phosphoglyceric acid + $Co\mathrm{H}_2$ - phosphotriose—apo-dehydrogenase.

(*b*) Phosphotriose (phosphodihydroxyacetone) + $Co\mathrm{H}_2$ - phosphoglycerol - apo-dehydrogenase $\rightleftharpoons$ Phosphoglycerol + *Co*-phosphoglycerol–apo-dehydrogenase.

Different apo-dehydrogenases but the same co-dehydrogenase (co-zymase) are required for the two reactions. Evidence in support of this interpretation of the facts is that an extract can be prepared from brain which can effect the oxidation of phosphotriose to phosphoglyceric acid, but not its reduction to phosphoglycerol (absence of phosphoglycerol–apo-dehydrogenase) or the oxido-reduction of phosphoglycerol and pyruvic acid (Adler and Hughes, *l.c.*). In such an extract the presence of the phosphotriose dehydrogenase can be demonstrated by the reduction of Methylene Blue when diaphorase (p. 34) is added and the production of $Co\mathrm{H}_2$ (Eq. *a* in the scheme on p. 33*b*) can be demonstrated spectroscopically. In muscle extract which contains all three dehydrogenases the $Co\mathrm{H}_2$ is rapidly dehydrogenated and cannot be detected spectroscopically.

It has been already stated that in all these reactions it is the complex of co-dehydrogenase and apo-dehydrogenase which reacts with the substrate.

In contrast with this "two enzyme theory" of the mechanism of this reaction, is the opinion held by Green and his colleagues (Dewan and Green, Biochem. J. 1937, **31**, 1074; 1938, **32**, 626; Green, Needham and Dewan, *ibid.* 1937, **31**, 2327; Straub, Corran and Green, Nature, 1939, **143**, 119), who consider that the dismutation is effected by a single enzyme, *phosphotriosemutase*, which probably has two active centres.

The experiments of Quastel and Wheatley (Biochem. J. 1938, **32**, 936) on the enzymic reduction of K ferricyanide by various substrates in presence of muscle extract afford very strong evidence against the existence of specific mutases for these reactions.

3. *Oxido-Reduction of Phosphoglyceraldehyde and Acetaldehyde.*—The question of the enzymic transference of hydrogen from phosphoglyceraldehyde to acetaldehyde in presence of co-zymase *Co* I was studied (von Euler, Alder and Kyrning, Z. physiol. Chem. 1936, **242**, 215) by examining various apo-dehydrogenase preparations from yeast by means of the Methylene Blue technique for their ability in presence of co-zymase to activate alcohol, phosphotriose and hexosediphosphate. It was thus found that different apo-dehydrogenases are required for the reactions with alcohol and phosphotriose. Hexosediphosphate only reacts in these conditions when zymohexase (aldolase) is present, which produces phosphotriose from it enzymically.

An apo-dehydrogenase specific to the alcohol reaction and inactive towards phosphotriose can be prepared by autolysing bottom yeast in presence of ethyl acetate and partially precipitating with alcohol. A solution of this precipitate in water is then treated with 3 vol. saturated ammonium sulphate solution and the precipitate dissolved in water and dialysed. An apo-dehydrogenase for the phosphotriose reaction has so far been obtained only as a mixture with the alcohol-apo-dehydrogenase.

In the light of these experiments von Euler (Ergebn. Physiol. 1936, **38**, 1; von Euler, Adler and Hellström, Svensk Kem. Tidskr. 1935, **47**, 290; Z. physiol. Chem. 1936, **241**, 239) suggested that the oxido-reduction of phosphotriose and acetaldehyde to phosphoglyceric acid and alcohol might take place in the following stages. D^T is the apo-dehydrogenase specific to phosphotriose; D^A that specific to alcohol; $R.CHO$ is phosphotriose; F flavin enzyme; co-zymase (*Co*) is the dissociable prosthetic group of both of these apo-dehydrogenases and is distributed between them.

1. $R{\cdot}CHO + H_2O + D_T\mathit{Co} \rightleftharpoons R{\cdot}COOH + D^T\mathit{Co}H_2$
2. $D^T\mathit{Co}H_2 + F \rightleftharpoons D^T\mathit{Co} + FH_2$.
3. $D^A\mathit{Co} + FH_2 \rightleftharpoons D^A\mathit{Co}H_2 + F$.
4. $D^A\mathit{Co}H_2 + CH_3{\cdot}CHO \rightleftharpoons D^A\mathit{Co} + CH_3{\cdot}CH_2{\cdot}OH$

The intervention of the flavin enzyme is not accepted by all workers (*see* Warburg, Die Umschau, 1938, Heft 2), and in view of later work its place should perhaps be taken by diaphorase (*see below*).

OXIDO-REDUCTION OF PHOSPHOTRIOSE AND PYRUVIC ACID.—The changes which occur in lactic acid formation in muscle extract may probably be formulated in a similar manner to those in yeast preparations just described, substituting pyruvic acid and lactic acid for acetaldehyde and alcohol. Co-zymase and two apo-dehydrogenases appear to be involved—phosphotriose—and lactic—apo-dehydrogenase.

OXIDO-REDUCTION OF PHOSPHOGLYCEROL AND PYRUVIC ACID, yielding phosphotriose and lactic acid, is of importance in the process of lactic acid formation in muscle extract and is to be formulated on similar lines to the oxido-reduction of phosphotriose and pyruvic acid, co-zymase and two distinct apo-dehydrogenases—phosphoglycerol—and lactic—apo-dehydrogenases—being involved (*see* Adler, von Euler and Hughes, Z. physiol. Chem. 1938, **252**, 1).

The reactions which occur in yeast preparations are similar to those which occur in muscle extract, but as already explained (p. 3), phosphoglycerol does not appear to react with acetaldehyde but is rapidly hydrolysed with formation of glycerol and phosphoric acid (*see* Adler and Günther, *ibid.* 1938, **253**, 143).

DIAPHORASE.—(*Green's co-enzyme factor.*) The dehydrogenation of $\mathit{Co}H_2$ cannot be directly effected by such hydrogen acceptors as Methylene Blue or molecular oxygen, but proceeds by way of a specific enzyme which is present in muscle extract and is termed diaphorase by von Euler, *co-enzyme factor* by Green (Adler, von Euler and Hellström, Arkiv Kemi, Min., Geol. 1937, **12**, B, No. 38; Adler, von Euler and Hughes, Z. physiol. Chem. 1938, **252**, 1; Dewan and Green, Nature, 1937, **140**, 1097; Green, Dewan and Leloir, Biochem. J. 1937, **31**, 76). Its specific function is to transfer the hydrogen of $\mathit{Co}H_2$ to cytochrome or Methylene Blue, etc. According to Straub, Corran and Green (Nature, 1939, **143**, 119) it is a flavoprotein, found also in heart muscle (Straub, *ibid.* 76), the prosthetic group of which is a flavin-adenine dinucleotide. Warburg's *yellow enzyme*, which is a flavoprotein, the prosthetic group of which is phospholactoflavin (phospho-6:7-di-methyl-9-*d*-1′-ribityl-*iso*alloxazine; *see* Karrer and Meerwein, Helv. Chim. Acta, 1936, **19**, 264) discharges a similar function, but is much less efficient than dia-phorase.

Another enzyme of analogous properties (distinguished as *diaphorase II*) is present in many animal tissues and dehydrogenates $\mathit{Co}\text{II}\,H_2$ and transfers the hydrogen to Methylene Blue or cytochrome (Adler, von Euler and Günther, Nature, 1939, **143**, 641).

FUNCTION OF CO-ZYMASE IN LACTIC ACID FORMATION IN MUSCLE EXTRACT.—Until recently no experimental evidence had been obtained of the intervention of a co-dehydrogenase in the production of lactic acid in muscle extract, although the nature of the changes involved (oxido-reduction of pyruvic acid and phosphotriose yielding lactic acid and phosphoglyceric acid) rendered it probable, from analogy with alcoholic fermentation, that such a co-enzyme was present. Dialysed muscle extract (+adenylic acid+ Mg) converted glycogen into lactic acid without the addition of a dehydrogenase (*see* Lohmann, Biochem. Z. 1931, **241**, 50). Very prolonged dialysis irreversibly inactivated the enzymes so that the faculty of converting glycogen into lactic acid could not be restored.

It has since been found (Meyerhof and Ohlmeyer, Naturwiss. 1936, **24**, 741; Biochem. Z. 1937, **290**, 334) that prolonged dialysis of muscle extract (36–48 hours) renders it incapable of bringing about the oxido-reduction of pyruvic acid and phosphotriose (or of hexosediphosphate in presence of zymohexase) either alone or in presence of adenylic acid and magnesium. The addition of co-zymase restores the activity completely. As little as 0·4 μg. of a 40% active "co-zymase" restored 10%, 5 μg. 50% and 150 μg. the whole of the original activity. All these experiments were carried out in presence of NaF to prevent the further decomposition of the phosphoglyceric acid.

von Euler and his colleagues (Adler, von Euler and Hellström, Nature, 1936, **138**, 968; von Euler, Adler and Günther, Arkiv Kemi, Min., Geol. 1936, **12**, B, No. 31; von Euler, Adler, Günther and Hellström, Z. physiol. Chem. 1937, **245**, 217) have confirmed these observations and have also shown by direct spectroscopic measurements that *Co* and $\mathit{Co}H_2$ take part (*a*) in the reversible action of heart-muscle dehydrogenase on lactic acid, for which a co-enzyme was known to be necessary (*cf.* Green and Brosteaux, Biochem. J. 1936, **30**, 1489); (*b*) in skeletal muscle extract in the reversible dehydrogenation of lactic acid and in the reduction of phosphoglyceraldehyde to phosphoglycerol.

Phosphorylation

1. PHOSPHORYLATION BY THE ADENYLIC ACID SYSTEM IN LACTIC ACID FORMATION.—After Lohmann's (Biochem. Z. 1931, **237**, 445) discovery that the readily dialysable co-enzyme of lactic acid formation in muscle extract consisted of two parts (*see* p. 18*b*): (*a*) magnesium, (*b*) adenylpyrophosphate (adenosinetriphosphate), it was early suggested (Meyerhof and Lohmann, Naturwiss. 1931, **19**, 375; Biochem. Z. 1932, **253**, 431) that the

esterification by phosphoric acid (phosphorylation) which precedes the decomposition of the carbohydrate in lactic acid formation is accompanied by a partial dephosphorylation of the adenylpyrophosphate, which is resynthesised in the further course of the reaction. Evidence that this was actually the case gradually accumulated (for reference to early instances of this kind, *see* Meyerhof and Kiessling, Biochem. Z. 1935, **283**, 106).

The next positive step was made by Lohmann (*ibid.* 1934, **271**, 264), who showed that in dialysed muscle extract phosphoric acid groups were transferred from phosphocreatine to adenylic acid yielding adenylpyrophosphate and creatine:

2 Phosphocreatine + Adenylic acid
→ 2 Creatine + Adenylpyrophosphate.

The next important advance was made by Parnas and his colleagues. Parnas was led to these investigations by observations on the production of ammonia in muscle pulp. The origin of the ammonia was traced to the action of a specific *deaminase* on the adenylic acid formed by the partial dephosphorylation of adenylpyrophosphate by a *phosphatase* present in the muscle; the adenylpyrophosphate itself is not attacked by the deaminase:

Adenylic acid $\xrightarrow{\text{Deaminase}}$ Inosinic acid + NH_3

When conditions were favourable for the resynthesis of adenylpyrophosphate from the adenylic acid, the liberation of ammonia ceased. (For a general account of this work, *see* Parnas, Klin. Woch. 1935, **14**, 1017; Ergebn. Enzymforsch. 1937, **6**, 57.)

Parnas and his colleagues (Parnas and Ostern, Nature, 1934, **134**, 627; Parnas, Ostern and Mann, Biochem. Z. 1934, **272**, 64; 1935, **275**, 74) found that when adenylpyrophosphate was added to muscle pulp poisoned by iodoacetic acid, the adenylpyrophosphate was decomposed and deaminated; scarcely any phosphoric acid was liberated, but, as judged by the rate of hydrolysis of the products by N-HCl at 100, hexosediphosphate was formed. Hence the change which had occurred was presumed to be

Adenylpyrophosphate + glycogen
→ Adenylic acid + Hexosediphosphate
Adenylic acid → Inosinic acid + NH_3

The decomposition of the adenylic acid under these conditions was stopped by the addition of phosphoglyceric acid, and adenylpyrophosphate and phosphocreatine were then found to be present. Hence it was presumed that the phosphoric group of phosphoglyceric acid, or of some closely related derivative (subsequently found to be phosphopyruvic acid, Parnas, Ostern and Mann, Biochem. Z. 1935, **275**, 163), was transferred to creatine and adenylic acid. Whether the phosphorylation of creatine was direct or indirect was not at first determined, but this information was subsequently supplied independently and almost simultaneously by a number of workers (Ostern, Baranowski and Reis, *ibid.* 1935, **279**, 985; Lehmann, *ibid.* 1935, **281**, 271; Meyerhof and Lehmann, Naturwiss. 1935, **23**, 337; Needham and van Heyningen, Biochem. J. 1935, **29**, 2040; Nature, 1935, **135**, 585), who found that adenylic acid was essential for the change, whereas creatine alone had no effect and was not phosphorylated unless adenylic acid were present.

(1) 2 Phosphopyruvic acid + Adenylic acid
→ 2 Pyruvic acid + Adenylpyrophosphate.
(2) Adenylpyrophosphate + 2 Creatine
→ Adenylic acid + 2 Phosphocreatine.

Reaction 2 is the reverse of Lohmann's reaction and it appears that the reaction is reversible, an equilibrium being in all cases attained.

The importance of the observations made by Parnas and his colleagues lay in the fact that they proved that the adenylpyrophosphate was reconstituted during the glycolysis from the adenylic acid formed at another stage of the decomposition (*see* equations 1 and 2, p. 18*b*).

Phosphorylation and Fermentation of Hexoses in Muscle Extract.—Muscle extract, prepared by extracting rabbit or frog muscle in the cold with water or KCl solution, rapidly converts glycogen into lactic acid in presence of phosphate, hexosephosphoric esters, chiefly the diphosphate, accumulating as in the alcoholic fermentation of glycogen by yeast preparations (p. 36*b*). The extract only attacks the fermentable hexoses slowly, but in the presence of a thermolabile activator (*hexokinase*), obtained from autolysed yeast by precipitation with alcohol, it rapidly converts added hexoses in the presence of phosphate into lactic acid (Meyerhof, Biochem. Z. 1927, **183**, 176). Hexokinase has been found to be an *apo-phosphorylase*, capable of catalysing the transference of phosphate from adenylpyrophosphate to the hexoses, with formation of hexosemonophosphate (Meyerhof, Naturwiss. 1935, **23**, 850), which is readily attacked by the muscle enzyme.

Phosphorylation by the Adenylic Acid System in Alcoholic Fermentation.—Adenylpyrophosphate has been isolated from yeast in the pure state Wagner-Jauregg, Z. physiol Chem. 1936, **238**, 129; *see also* von Euler, Adler and Pétursson, Svensk Kem. Tidskr. 1935, **47**, 249). It probably occurs in fresh yeast in the form of diadenosine-5-5′-tetraphosphoric acid (Meyerhof and Kiessling, Naturwiss. 1938, **26**, 13). The adeninenucleotide (yeast adenylic acid) formed by the hydrolysis (enzymic or otherwise) of yeast nucleic acid is adenosine-3-phosphoric acid and has no co-enzymic activity. It is rapidly hydrolysed by a phosphatase present in yeast to form adenosine and phosphoric acid. This adenosine is converted into adenosine-5-phosphoric acid (muscle adenylic acid), not the original 3-phosphoric acid, by treatment in presence of yeast extract with hexosediphosphate and phosphoric acid (oxido-reductive phosphorylation) or with phosphoglyceric acid. (Ostern and Terszakowec, Z. physiol. Chem. 1937, **250**, 155; Ostern, Baronowski and Terszakowec, *ibid.* 1938, **251**, 258; Ostern, Terszakowec and St. Hubl. *ibid.* 1938, **255**, 104.)

It was shown independently and almost simultaneously by Lutwak-Mann and Mann (Biochem. Z. 1935, **281**, 140) and, less definitely, by von Euler and Adler (Arkiv Kemi, Min., Geol. 1935, **12**, B, No. 12) that adenylic acid added to yeast preparations played essentially the same part as in muscle extract in the transference of the phosphate group from phosphopyruvic acid to glucose. The former workers, by the use of a fixation method, demonstrated the production of pyruvic acid in the reaction. They also showed that when added to hexosediphosphate in yeast-maceration extract adenylic acid was converted into adenylpyrophosphate and conversely that the pyrophosphate added to glucose yielded hexosediphosphate.

Adenylpyrophosphate+glucose $\rightleftharpoons$ adenylic acid +hexosediphosphate.

This last reaction they regarded as the starting point of alcoholic fermentation.

According to Ostern and his colleagues (*l.c.*) muscle adenylic acid may function in the transfer of phosphate groups in yeast preparations either by cyclic conversion into adenosine, or by being further phosphorylated to adenosinediphosphoric acid and adenosinetriphosphoric acid (adenylpyrophosphate). In muscle extracts the dephosphorylation of adenylpyrophosphate does not proceed below the adenosinemonophosphate (adenylic acid) stage and under some conditions only goes as far as adenosinediphosphoric acid (*see* Meyerhof, Schulz and Schuster, Biochem. Z. 1937, **293**, 309). Under suitable conditions adenosine, adenosinephosphoric acid and adenosinediphosphoric acid can all act as phosphate acceptors; the mono-, di and tri-phosphoric acids as donators.

PHOSPHORYLATION BY INORGANIC PHOSPHATE.—All the cases of phosphorylation so far considered have involved the transference of phosphate from one compound to another without any increase in the total amount of combined phosphorus. There are several reactions, however, in the processes of alcoholic fermentation and lactic acid formation by preparations of yeast or muscle in which inorganic phosphate is esterified.

1. *Phosphorolysis of Glycogen: A. In Muscle Extract.*—When glycogen and inorganic phosphate are added to muscle extract which has been submitted to autolysis and dialysis, glycogen and inorganic phosphate disappear and hexosemonophosphate (Embden ester) is formed (Ostern, Guthke and Terszakowec, Z. physiol. Chem. 1936, **243**, 9). The method may be used for the preparation of hexosemonophosphate, but unless care is taken the product may contain glycogen. The addition of adenylpyrophosphate or phosphocreatine is not required for the reaction, and under the foregoing conditions it only occurs with glycogen and not with glucose or fructose.

Parnas (*see* Ergebn. Enzymforsch. 1937, **6**, 57) regards the process as a phosphorolysis in which phosphoric acid plays the part played by water in hydrolysis. There is no indication of the intermediate formation of glucose or any other hexose. Muscle, however, contains an active amylase (*see* Willstätter and Rohdewald, Compt. rend. Trav. Lab. Carlsberg, 1938, **22**, 553) so that the possibility of amylase action has to be considered.

If adenylpyrophosphate is added to the mixture in which hexosemonophosphate has been produced, a further reaction, which is not inhibited by iodoacetic acid, occurs and the hexosemonophosphate is converted into hexosediphosphate

2 Hexosemonophosphate + Adenylpyrophosphate $\rightarrow$ 2 Hexosediphosphate + Adenylic acid.

Confirmatory evidence that the formation of hexosediphosphate in muscle extract takes this indirect course is furnished by the effect on the process of phloridzin, which inhibits the formation of the monophosphate much more strongly than its further phosphorylation. Hence in autolysed and dialysed muscle extract containing monoiodoacetic acid and phloridzin no hexosemonophosphate is formed from glycogen and phosphate, whereas when monophosphate and adenylpyrophosphate are added hexosediphosphate and adenylic acid (which becomes deaminated) are formed.

The role of co-enzymes in this reaction has been much discussed. Parnas at first (Ergebn. Enzymforsch. 1937, **6**, 57) held the view that no co-enzyme was required, but subsequently (Parnas and Mochnacka, Compt. rend. Soc. Biol. 1936, **123**, 1173) found that some muscle extracts could be inactivated by autolysis and dialysis and by other methods, and could then be reactivated by adenylpyrophosphate, adenylic acid or inosinic acid. von Euler also considers (Bauer, von Euler and Lundberg, Z. physiol. Chem. 1938, **255**, 89) that the adenylic acid system is required and in this he is supported by Kendal and Stickland (Biochem. J. 1937, **31**, 1758; 1938, **32**, 572). As regards the nature of the hexosemonophosphate formed, it seems probable that the first product is the non-reducing *Cori ester* (glucopyranose-1-phosphate; *see* p. 22*b*), a glycosidic linkage being first formed between the phosphoric acid and the hexose, and that, under the influence of a enzyme system, the action of which is greatly accelerated by magnesium ions, the phospho-group wanders to the 6-carbon atom, glucopyranose-6-phosphate being formed which in its turn passes into the equilibrium Embden ester (Cori, Colowick and Cori, J. Biol. Chem. 1937, **121**, 465).

It should be emphasized that of the hexosemonophosphates which are known to occur in the crude hexosemonophosphate obtained either in muscle extract or in yeast preparations, *i.e.* glucose-, mannose- and fructose-6-phosphate, only the last can be converted by direct phosphorylation into hexosediphosphate (fructose-1:6-diphosphate). Lohmann's *phosphohexomutase* (Biochem. Z. 1933, **262**, 1937), however, rapidly converts any one of these monophosphates into an equilibrium mixture of all three (*see* p. 22*a*). Hence, in presence of this enyzme, further phosphorylation of hexosemonophosphate may proceed in every case by way of fructose-6-phosphate.

B. *Phosphorylation of Glycogen and Hexoses by Yeast Preparations.*—In the fermentation of glycogen, present in or added to a yeast preparation, the relation between fermentation and esterification is different from that which obtains in glucose fermentation, the ratio of phosphoric ester produced to CO_2 evolved being much higher (*see also* p. 19*b*). In presence of fluoride, which completely inhibits the esterification of the hexoses, the fermentation (evolution of CO_2) of glycogen is almost completely inhibited, whereas esterification still goes on, although more slowly (70%), and hexosediphosphate accumulates along with phosphoglyceric acid and phosphoglycerol formed from the diphosphate. If acetaldehyde be present, phosphoglyceric acid is the main product of the oxido-reduction. In presence of NaF this oxido-reduction is catalysed by the hexosediphosphate produced from the glycogen.

Isolated observations were early recorded, which pointed to the probability that hexosemonophosphate was the primary product of the phosphorylation both of glycogen and hexoses by yeast preparations. Thus Nilsson (Arkiv Kemi, Min., Geol. 1930, **10**, A, No. 7) found that when washed dried yeast, free from co-zymase but containing glycogen, was treated with phosphate, hexosemonophosphate was formed. This reaction was inhibited by iodoacetate but not by fluoride (Nilsson, Zeile and von Euler, Z. physiol. Chem. 1931, **194**, 53).

According to Schäffner and his colleagues (*ibid.* 1935, **232**, 213; **234**, 146; 1936, **238**, 111; 1938, **251**, 144) the systems required for the phosphorylation of glucose and glycogen in yeast preparations are quite distinct and can be experimentally separated. Dialysed Lebedev extract phosphorylates glycogen without any addition of co-enzymes, but only phosphorylates glucose when co-zymase and Mg are added, and when the coupled oxido-reduction of phosphotriose occurs simultaneously. One component of the Lebedev extract which is essential for the phosphorylation of glucose is very sensitive to alkali (p_H 8·6), but this component is not required for the phosphorylation of glycogen. The product in both cases is hexosemonophosphate.

2. Phosphorylation of Mannose by Yeast Preparations.—It has been found (Jephcott and Robison, Biochem. J. 1934, **28**, 1844) that when dried yeast acts on mannose at 38° only a comparatively small proportion of hexosediphosphate is produced and the large monophosphate fraction consists almost entirely of mannose-6-phosphate, whereas at 25° more hexosediphosphate is formed and the monophosphate fraction contains more glucose- and fructose-phosphates. A suggested explanation, which requires further experimental confirmation, is that normally mannosemonophosphate is the first product, but passes, under the influence of Lohmann's phosphohexomutase (p. 22*a*) into a form which is converted by direct phosphorylation into hexosediphosphate. At the higher temperature the action of this enzyme may be supposed to be inhibited and the mannose monophosphate remains unchanged.

Direct evidence that in the fermentation of glucose by yeast preparation the formation of hexosemonophosphate precedes that of the diphosphate was obtained by Meyerhof (Biochem. Z. 1934, **27**, 380) by estimating the amounts of the two esters at intervals during the first 20 minutes of the fermentation. It was also found that the esterification preceded the evolution of CO_2 (*see also* Boyland, Biochem. J. 1929, **23**, 219; 1930, **24**, 7).

The interesting hypothesis that the first stage in the fermentation of sugars by yeast is their condensation to glycogen which is subsequently converted into alcohol and CO_2 has been supported by Willstätter and Rohdewald (Z. physiol. Chem. 1937, **247**, 269) mainly on the ground that when yeast is added to a solution of glucose, a definite amount of the sugar disappears from the solution before fermentation can be detected and this amount can be recovered from the washed yeast by hydrolysis with acid or by Pflüger's method. However, the differences mentioned above between the phenomena of fermentation of glycogen and of glucose provide a strong argument against Willstätter and Rohdewald's explanation of their observations (*see also* Myrbäck, Örtenblad and Ahlborg, Enzymologia, 1937, **3**, 210); Goda, Biochem. Z. 1938, **298**, 431).

3. Phosphorylation of Glucose by Inorganic Phosphate in Presence of Phosphotriose, Acetaldehyde and Traces of Hexosediphosphate.—This is the main reaction in which esterfication is effected by inorganic phosphate (Equation η in Meyerhof's scheme). It has already been discussed on p. 30, where it was shown (*a*) that the presence of a co-phosphorylase was essential, and (*b*) that the esterification of the phosphate was coupled with oxido-reduction of phosphotriose and acetaldehyde.

This reaction has been intensively studied by Needham and Pillai (Biochem. J. 1937, **31**, 1837) and by Meyerhof and his colleagues (Biochem. Z. 1937, **293**, 309; 1938, **297**, 90, 113). The former workers found that in an aqueous extract of the acetone-powder prepared from muscle extract the esterification of adenylic acid (*AA*) by inorganic phosphate to form adenylpyrophosphate (*ATP*; adenosine triphosphate) was coupled with the oxido-reduction of phosphotriose and pyruvic acid (yielding phosphoglyceric acid and lactic acid) and did not proceed unless oxido-reduction occurred simultaneously. The phosphorylation could be coupled with several other oxido-reductions: dismutation of phosphotriose, oxido-reduction of phosphotriose and oxaloacetic acid or of phosphoglycerol and pyruvic acid but not of glyceraldehyde and pyruvic acid or oxaloacetic acid.

Meyerhof, working with a restricted system of enzymes based on the employment of the B protein from yeast (*see* p. 29*b*), has found that in these conditions the coupled reactions are the esterification of adenosine-diphosphate (*ADP*), not *AA*, by inorganic phosphate, yielding *ATP*, and the union of co-zymase with hydrogen, derived most probably from the phosphoglyceraldehyde form of phosphotriose, yielding phosphoglyceric acid and dihydro-co-zymase:

(1) $ADP + H_3PO_4 \rightleftharpoons ATP$;

(2) $Co +$ phosphoglyceraldehyde $\rightleftharpoons CoH_2 +$ phosphoglyceric acid;

or summarised:

(3) $ADP + H_3PO_4 + Co +$ phosphoglyceraldehyde $\rightleftharpoons ATP + CoH_2 +$ phosphoglyceric acid.

When glucose is present a further reaction occurs and ADP is reformed along with hexosemonophosphate:

(4) $ATP +$ glucose $\rightarrow ADP +$ hexosemonophosphate.

The reaction represented by the summarised equation (5):

(5) $ADP + H_3PO_4 +$ phosphoglyceraldehyde $+ Co +$ glucose $\rightarrow ATP +$ phosphoglyceric acid $+ CoH_2 +$ hexosemonophosphate

proceeds in presence of B protein until practically the whole of the co-zymase is reduced. The reduction of co-zymase by alcohol (or lactic acid) and the dehydrogenation of CoH_2 by acetaldehyde (or pyruvic acid) are not coupled with phosphorylation.

Reactions (1), (2) and (3) are reversible. Direct experimental evidence has been obtained that in the presence of protein B from yeast, phosphoglyceric acid and reduced co-zymase react to form phosphotriose and co-zymase and that this change is coupled with the liberation of one PO_4 group from ATP, yielding ADP. Mixtures made up ($10^{-5}M$) to correspond with the molecular quantities in the two sides of equation (3) attain approximately the same equilibrium (2/3 of Co and 1/3 of CoH_2), and this is affected by excess of any of the constituents in general agreement with the law of mass action. As the active mass of some of the components (*e.g.* co-zymase, phosphoglyceraldehyde) may differ very materially from the amounts added, no very close agreement can be expected.

When the amount of Co present is diminished to catalytic proportions and alcohol is added the following reaction (6) occurs:

(6) Phosphoglyceric acid + alcohol $+ ATP \rightarrow$ Phosphotriose + aldehyde $+ ADP + H_3PO_4$.

If KCN is used as a fixative for phosphotriose the reaction represented by equation (3) read from right to left goes almost to completion, as does also the reaction corresponding with equation (6).

As regards the energy relations of the coupled reaction, it is pointed out by Meyerhof that the induced (endothermic) phosphorylation of ATP is rendered possible by the spontaneous (exothermic) oxido-reduction of phosphoglyceraldehyde and co-zymase, whilst in the reverse reaction the induced reduction of phosphoglyceric acid and dehydrogenation of CoH_2 are rendered possible by the energy derived from the spontaneous hydrolysis of ATP, yielding ADP and phosphoric acid (+11,000 g.-cal.).

Phosphorylation by Co-zymase.—Much work has been done on this subject without a definite result having been obtained. The earlier investigations all tended to show that co-zymase could replace adenylic acid both in muscle and yeast preparations and that it played a similar part to adenylic acid in aiding the transference of phosphate (von Euler and Günther, Z. physiol. Chem. 1935, **235**, 104; **237**, 221; 1936, **239**, 83; von Euler and Vestin, *ibid.* 1935, **237**, 1; Vestin, *ibid.* 1936, **240**, 99; von Euler and Adler, Arkiv Kemi, Min., Geol. 1935, **12**, B, No. 12). A remarkable feature of these experiments was that co-zymase which had been heated with 0·03 N-$NaOH$, and thereby inactivated as regards the initiation of alcoholic fermentation, was still able to replace adenylic acid and was even more active than the original untreated preparation. These properties were shown by very highly concentrated preparations of co-zymase ($ACo = 400{,}000$).

More recent work, however, showed (von Euler *et al*, Arkiv Kemi, Min., Geol. 1936, **12**, B, No. 24) that co-zymase could be prepared (p. 16c) in a higher state of purity than had previously been attained, and that in this form it was unable to replace adenylic acid until it had been treated with alkali.

This apparent inactivity of pure co-zymase has been found (Ohlmeyer and Ochoa, Biochem. Z. 1937, **293**, 338) to be due to the presence in the experimental mixtures of Na ions (*cf.* Harden, Biochem. J. 1913, **7**, 214) which inhibit the transference of PO_4 from phosphopyruvic acid to glucose by co-zymase and, to a less extent, by adenylic acid. If Mn is added, this inhibitory effect is removed and the co-zymase becomes about half as active in the transfer of PO_4 as is adenylic acid under the same conditions, without losing more than 5% of its activity as a dehydrogenase. Hexahydro-co-zymase (CoH_6), which is inactive as a co-dehydrogenase, behaves as a phosphorylase in a similar manner to the unreduced co-zymase but is even more active, equalling adenylic acid. The inhibiting effect of Na is also removed by Mg, NH_4 and K, the relative efficiencies (atomic) being $Mn:Mg:NH_4:K$ as 1:50: 1,000:2,000. In the absence of glucose, the production of readily hydrolysable P can be detected, but only about 10% of the co-zymase appears to be phosphorylated. "Co-zymase-pyrophosphate" has been isolated as a Ba salt (Meyerhof and Kiessling, Naturwiss. 1936, **24**, 361, 557), but its constitution has not yet been determined.

The increase in activity caused by treatment with alkali (which is known to remove the nicotinamide group of the co-dehydrogenase) is almost certainly due to the formation of a phosphorylating compound, and such a compound has been isolated from the products of the action of alkali (Schlenk and von Euler, Arkiv Kemi, Min., Geol. 1936, **12**, B, No. 20); it is probably a compound of adenine with 2 molecules of ribosephosphate, but its constitution is not yet known (*see* von Euler, Ergebn. Physiol. 1936, **38**, 1). In the light of the foregoing observations it may be taken provisionally that pure co-zymase in the presence of a sufficiency of Mn and Mg ions is able to act as a co-phosphorylase both in muscle and yeast preparations, but the mechanism of the reactions is not yet known with certainty.

In this connection great interest attaches to the observations of von Euler and his colleagues (von Euler, Adler and Steenhoff Eriksen, Z. physiol. Chem. 1937, **248**, 227; von Euler and Adler, *ibid.* 1938, **252**, 41; Vestin, Naturwiss. 1937, **25**, 667; von Euler and Vestin, Arkiv Kemi, Min., Geol. 1936, **12**, B, No. 44; von Euler and Bauer, Ber. 1938, **71** [B], 411) who have found that co-zymase (co-dehydrogenase I) and co-dehydrogenase II can each be converted into the other by yeast preparations. Thus when co-dehydrogenase II (free from co-zymase) is added to the apo-zymase system used for testing co-zymase, fermentation sets in after a prolonged induction period. The boiled filtrate from such an experiment is immediately active in the test showing the presence of co-zymase. The reverse change also occurs, as judged by the Warburg and Christian test for co-dehydrogenase II, but the evidence is not so satisfactory as in the former case. von Euler (*see* article in "Hyllningskrift till Bertil Almgren På Sextioårsdagen," Stockholm, 1938, p. 281) makes the interesting suggestion (which requires further experimental investigation), that phosphorylation by co-zymase may be due to this reversible change.

$$Co\text{I} + H_3PO_4 \rightleftharpoons Co\ \text{II}$$

FERMENTATION OF HEXOSEDIPHOSPHATE IN PRESENCE OF ADENYLIC ACID.—The rate of fermentation of hexosediphosphate can be increased approximately to that of glucose by simple addition of adenylic acid (Ohlmeyer, Biochem. Z. 1935, **283**, 114), whereas adenylpyrophosphate has practically no effect. The reactions involved are complex and not yet fully understood, but the essential feature seems to be the transference of phosphate to the adenylic acid with formation of adenylpyrophosphate and hexosemonophosphate.

2 Hexosediphosphate + adenylic acid → adenylpyrophosphate + 2 hexosemonophosphate.

This is apparently coupled with a second reaction representing a rapid fermentation,

Hexosediphosphate + adenylic acid → adenylpyrophosphate + $2CO_2$ + 2 alcohol

but the exact mechanism of the change is not yet understood, particularly the part played by the hexosemonophosphate. The reaction only proceeds rapidly as long as adenylic acid is present as there is no mechanism for the dephosphorylation of the adenylpyrophosphate produced. The comparatively slow rate of fermentation of hexosediphosphate by yeast preparations is attributed to the fact that the adenylic acid necessary for the fermentation can, under these conditions (absence of a PO_4 receptor), only be reformed from the adenylpyrophosphate by enzymic hydrolysis (*see* Lutwak-Mann and Mann, Biochem. Z. 1935, **281**, 140), a slow process, and not by transference of the phosphate as in the fermentation of glucose.

FERMENTATION OF HEXOSEDIPHOSPHATE AND GLUCOSE IN PRESENCE OF ARSENATE.—The mechanism of this remarkable reaction (*see* p. 20*a*) is even yet not fully understood. The rate of conversion of hexosediphosphate in presence of acetaldehyde and fluoride into phosphoglyceric acid is increased about 20 times by arsenate (Meyerhof, *ibid.* 1934, **273**, 80), and the rate of decomposition of phosphopyruvic acid in absence of glucose is similarly increased (Meyerhof and Kiessling, *ibid.* 1935, **280**, 99). Experiments with the restricted system of Warburg and Christian (Meyerhof, Kiessling and Schulz, *ibid.* 1937, **292**, 25) show that in absence of protein A and in presence of protein B and 10^{-4} to 10^{-5} *M* arsenate, hexosephosphate is very rapidly oxidised to phosphoglyceric acid (Equation A).

A. Hexosediphosphate ($\rightleftharpoons$ phosphotriose) + 2 acetaldehyde → 2 phosphoglyceric acid ($\rightleftharpoons$ phosphopyruvic acid) + 2 alcohol.

Adenylic acid, Mg and Mn can all be omitted. When these factors and protein A are added the phosphoglyceric acid is rapidly decomposed (Equation B).

B. 2 Phosphoglyceric acid ($\rightleftharpoons$ phosphopyruvic acid) → 2 pyruvic acid + $2H_3PO_4$.

Reaction B, however, does not proceed unless hexosediphosphate is present along with an active oxido-reduction system. Added adenylic acid is converted into adenylpyrophosphate, but the dephosphorylation of this is not accelerated by arsenate under these conditions. The mechanism of this reaction is not yet understood.

Pillai (Biochem. J. 1938, **32**, 1087, 1961), who worked with a system of enzymes different from that used by Meyerhof, the dialysed extract of the acetone precipitate from muscle extract, has obtained evidence that the fundamental reaction in the acceleration produced by arsenate is the rapid dephosphorylation of adenylpyrophosphate yielding adenylic acid and inorganic phosphate. This occurs in the absence of adenylpyrophosphatase but requires the presence of co-zymase and traces of phosphoglyceric acid (the decomposition of which was prevented in Pillai's experiments by the addition of sodium fluoride). The function of the phosphoglyceric acid is not yet understood.

It has been pointed out (*see* Meyerhof, Kiessling and Schulz, Biochem. Z. 1937, **292**, 25; Meyerhof, Ohlmeyer and Möhle, *ibid.* 1938, **297**, 90; Needham and Pillai, Biochem. J. 1937, **31**, 1837) that the fundamental effect of arsenate is to annul the esterification of adenylic acid (or adenosinediphosphate) by inorganic phosphate, which in the absence of arsenate is coupled with the reduction of *Co*, without at the same time lowering the rate of this reduction. The change is represented by the equation Phosphotriose + *Co* → Phosphoglyceric acid + $Co\text{H}_2$ which is in agreement with the experimental result that no phosphoric esters accumulate. How the rapid rate of hydrogenation of *Co* is maintained is not yet understood. In the absence of arsenate this rapid rate is only observed when the coupled esterification of adenylic acid (or *ADP*) occurs. The dehydrogenation of $Co\text{H}_2$ by acetaldehyde is not affected by arsenate (Meyerhof, Ohlmeyer and Möhle, Biochem. Z, 1938, **297**, 90).

THE NATURE OF THE PROCESS OF FERMENTATION IN THE LIVING YEAST CELL.—When the fermentation effects produced by yeast preparations are compared with those due to living yeast cells, three main points of difference appear: (*a*) The basal rate of fermentation by the preparations is much lower than that characteristic of the cell. (*b*) The rate of fermentation of the preparations is greatly increased by the addition of phosphate (or arsenate) whereas that of the living cell is unaffected by these substances.

(*c*) The high rate of fermentation by the preparations in presence of phosphate is accompanied by the progressive accumulation of hexosephosphoric esters in stoichiometric proportion to the amount of sugar fermented. This does not occur and in fact is impossible in the living cell owing to the small amount of P available.

It is only in the presence of arsenate (*see* p. 20*a*) that the results given by the preparations approach those characteristic of the cell—a continuous high rate of fermentation unaccompanied by the accumulation of hexosephosphoric esters.

When the fermenting powers of yeast juice or zymin are compared with those of living yeast it is found that yeast juice ferments glucose at a rate which is only about $\frac{1}{40}$ of that of the yeast from which it was prepared, whilst zymin ferments at a rate which is $\frac{1}{7}$–$\frac{1}{10}$ of that of yeast. In the presence of fructose and phosphate, the rate of fermentation of yeast juice may be increased as much as 20-fold, then amounting to about one-half the rate of that of living yeast, whilst that of zymin may be increased to approximately the same relative value. Similar relations exist in the cases of maceration extract and dried yeast. Assuming, as appears justified, that the process of fermentation is of the same general character in yeast as in yeast juice, it follows that yeast juice contains a large fraction of the fermenting complex present in yeast, but ferments hexosephosphates slowly and therefore regenerates inorganic phosphate slowly. Zymin appears to contain a somewhat smaller proportion of the fermenting complex, but has a much greater power of regenerating phosphate than yeast juice. An effect similar to that which is produced by grinding yeast, treating it with acetone or drying and heating it, is also produced, but to a smaller degree, by treating it with toluene (Harden) and various other substances (Kerr and Young, Austral. J. Exp. Biol. 1926, **3**, 177; Harden and Macfarlane, Biochem. J. 1930, **24**, 343) so that all these processes must result in some similar change which is rendered evident by the loss of the property of regenerating phosphate from hexosephosphate.

Of the nature of this change we are, at present, ignorant, but many facts strongly suggest that it is in some way due to the disorganisation of the cell.

The change in type of the fermentation can readily be observed when yeast is ground with sand and the ground mass directly tested at intervals with sugar and phosphate. As the grinding proceeds the basal rate with sugar gradually falls and the mass becomes progressively more sensitive to the action of phosphate (Harden and Macfarlane, Biochem. J. 1930, **24**, 343).

The lack of response by the living cell to phosphate and arsenate may possibly be due (*a*) to the selective permeability of the cell, or (*b*) to the existence in the cell of conditions for rapid fermentation which are already optimum so that the rate of fermentation is not affected by increase in the concentration of phosphate or by the presence of arsenate. The lack of progressive accumulation of hexosephosphates in the living cell implies either (*a*) that the cycle in the cell does not involve the formation of hexosephosphate esters by reactions β and δ of Meyerhof's scheme, or (*b*) that, if formed, they are decomposed at such a rate that no progressive accumulation occurs.

The striking effect of arsenate on fermentation by yeast preparations makes it impossible to reject the possibility that some labile accelerator with similar properties may be present in the cell and be inactivated when the cell is disintegrated or injured. No direct evidence of the existence of a substance of such properties has yet been obtained, but it must be recalled (*see* p. 39*a*) that in presence of a sufficient concentration of adenylic acid hexosediphosphate is fermented at the maximum rate (Ohlmeyer, Biochem. Z. 1935, **283**, 114). Meyerhof (Ergebn. Physiol. 1937, **39**, 54) draws attention to the possibility that in the living cell the adenylpyrophosphatase may be so active that a high fermentation of adenylic acid is maintained.

PHOSPHORYLATION IN LIVING YEAST. (*a*) *The Phosphorus Compounds of Yeast.*—Pressed brewer's yeast contains about 6 mg.P/g., 50% of which can be extracted with trichloroacetic acid (Macfarlane, Biochem. J. 1936, **30**, 1369). Of this, 15% is present as orthophosphate, 20% as a labile phosphoric acid containing inorganic pyrophosphate (*see* Lohmann, Biochem. Z. 1928, **202**, 466; Boyland, Biochem. J. 1930, **24**, 350) and 10% in organic combination. This last probably includes co-zymase, co-dehydrogenase II, adenylic acid and adenylpyrophosphate. A large part of the acid-insoluble fraction consists of a complex containing metaphosphoric acid (*see* Macfarlane, *l.c.*).

(*b*) *Changes in Distribution of* P *in the Yeast Cell during Fermentation.*—When fermentation is proceeding actively the acid-soluble orthophosphate decreases (*e.g.* from 1·05 mg. to 0·66 mg./g.), remains at the low level throughout the fermentation and returns approximately to the original level (0·93) when the sugar has been completely fermented, falling again if fresh sugar be added. What becomes of the orthophosphate P which disappears is not certainly known. It was however found, working with 100 g. yeast, that when the enzymic action was stopped during the fermentation by the addition of trichloroacetic acid, the filtrate contained hexosediphosphate (10 mg.P/100 g. yeast) which could be identified as the phenylhydrazine salt of phosphoglucosazone (Macfarlane, *ibid.* 1939, **33**, 565). When NaF (0·05*M*) was previously added, phosphoglyceric acid could be isolated, as much as 7 mg. of P being obtained in this form from 100 g. yeast.

These results afford conclusive evidence that definite changes in P distribution accompany fermentation in the living cell and that the same intermediate products are formed as in fermentation by yeast preparations. These facts render it extremely probable that the changes in the cell are of the same general character as those which occur in fermentation by yeast juice and other preparations. The exact cycle of events in the living cell and the reason for the difference between the intracellular and extracellular reactions remain to be discovered.

A. H.

FERMENTATION, BACTERIAL. INTRODUCTION.—Bacterial fermentation resembles yeast fermentation, including as it does the anærobic breakdown of hexose and related substances to simpler products; as all types of fermentation, with the exception of acetic, occur (or can occur) anærobically, the intermediate changes consist essentially of balanced oxidations and reductions; where two different molecules are concerned the process is termed an oxido-reduction, *e.g.*

dihydroxyacetonephosphate + acetaldehyde
= phosphoglyceric acid + ethyl alcohol;

where two similar molecules are concerned the process is called a dismutation:

2 dihydroxyacetonephosphate = 1 glycerolphosphoric acid+1 phosphoglyceric acid.

Other reactions are, (1) condensations between two molecules giving rise to 4-carbon compounds, *e.g.*

$$2CH_3{\cdot}CHO = CH_3{\cdot}CH(OH)CO{\cdot}CH_3$$

(2) decarboxylation of α-keto-acids,

$$CH_3{\cdot}CO{\cdot}COOH = CH_3{\cdot}CHO + CO_2.$$

The fermentation which has been studied most intensively is the alcoholic fermentation by yeast (*v.* FERMENTATION, ALCOHOLIC, this Vol., p. 8). The intermediate steps by which the process $C_6H_{12}O_6 = 2C_2H_5{\cdot}OH + 2CO_2$ occurs have been variously explained, the two principal theories being those of Neuberg and of Embden-Meyerhof-Parnas; the former held the field until 1934, when it was to a large extent superseded by the latter. As is seen in the article referred to, Neuberg's view regards methylglyoxal hydrate as the key product of the breakdown of the hexose molecule, and this may then be dismuted to glycerol and pyruvic acid, the latter decarboxylated to CO_2 and acetaldehyde. The $CH_3{\cdot}CHO$ may be either dismuted to ethyl alcohol and acetic acid or caused to undergo an oxido-reduction with methylglyoxal hydrate, giving either acetic acid and glycerol or ethyl alcohol and pyruvic acid. Neuberg extended his scheme to explain most bacterial fermentations, and his view has been developed by Kluyver and his school ("The Chemical Activities of Micro-organisms," University of London Press, 1931), the principal modification by the latter being the interpolation of a hypothetical phosphorylation prior to the primary disruption of the hexose.

The Embden-Meyerhof-Parnas scheme (*v.* this Vol. p. 32) postulates the oxido-reductions as occurring in phosphorylated molecules with adenylic acid and adenosine triphosphate as dephosphorylating and phosphorylating agents respectively. All the reactions postulated in this scheme have been shown to occur at high velocities in enzyme preparations from yeast juice, and the view that they represent the course of events with the intact yeast cell at present dominates fermentation chemistry. Accordingly great efforts are made to show that bacterial fermentations follow a similar path. This so far resolves itself into showing that bacteria can effect phosphorylations and can oxidise, reduce and dismute phosphorylated molecules. Actually the evidence that bacterial fermentations occur exclusively either by a modified Neuberg or by a modified Embden-Meyerhof-Parnas scheme is extremely fragmentary. For example, a given organism may produce lactic acid from methylglyoxal or from pyruvic acid+triosephosphate if conditions are suitable, yet either, both or neither of these paths may be followed during the disruption of hexose in fermentation. The problem has been attacked in the case of yeast by the use of "Lebedev" juice which contains the enzymes in a form in which co-enzymes, phosphate, etc., can be removed by dialysis, and the remaining enzyme system simplified by the use of specific inhibitors. Until recently no such preparation from bacterial cells had been made, and our knowledge of bacterial fermentation has been therefore limited to the use of intact cells; this severely restricted the study of the intermediate steps. Bacterial cells can, however, now be disrupted by a crushing mill and cell-free preparations of enzymes obtained (Booth and Green, Biochem. J. 1938, **32**, 855).

The products of bacterial fermentations are more varied than those resulting from the activity of yeast; it is usual for a fermentation to take its name from its characteristic end product, as, for example, "lactic," "propionic," "acetone" and "acetic" fermentations, each being brought about by closely related strains of special organisms. Only the main types of bacterial fermentation will be considered here.

Lactic Fermentation.—The simplest type of fermentation is that in which 1 mol. of hexose produces 2 mol. of lactic acid. When organisms effecting such a reaction can also hydrolyse lactose, they can be employed in the cheese industry, as, for example, *S. lactis* and *B. casei*. Several pathogenic members of the *Coccaceæ* such as the *gonococcus*, hæmolytic *streptococci* and *pneumococci* produce lactic fermentations. The course of the breakdown of glucose to lactic acid is not clear; at least two lactic fermenters have been shown to convert methylglyoxal to lactic acid in high yield; as non-lactic fermenters (*e.g. Bact. coli*) do the same thing, it does not provide strong evidence that normal fermentation proceeds by this route. Evidence of lactic fermentation taking a phosphorylation course has been provided in the case of *B. casei* by Virtanen and Tikka (Biochem. Z. 1930, **228**, 407).

Propionic Fermentation.—A fermentation in which propionic acid is the characteristic product is due to organisms present in Gruyère and Emmentaler cheeses. Fitz (Ber. 1878, **11**, 1890; 1879, **12**, 474; 1880, **13**, 1309) originally showed that *B. acidi propionici* produced acetic and propionic acids not only from glucose but also from malic and lactic acids. In the cheeses mentioned above propionic fermentation is a secondary fermentation of the lactic acid produced in the primary fermentation of lactose (*v.* Freudenreich and Orla Jensen, Zentr. Bakt. II, 1907, **17**, 529).

Quantitative studies by both the above investigators show that fermentation proceeds according to the equation

$$3CH_3{\cdot}CH(OH)COOH = 2CH_3{\cdot}CH_2{\cdot}COOH + CH_3{\cdot}COOH + CO_2 + H_2O$$

The CO_2 evolved accounts for the "eyes" found in the cheeses mentioned above. Besides lactic acid, glucose, fructose, mannose and lactose are fermented according to the same scheme (Virtanen, Acta Soc. Sci. Fennicæ Comment. Physico-Math., 1923, **1**, 36). Pyruvic acid is fermented as follows:

$$3CH_3{\cdot}CO{\cdot}COOH+H_2O$$
$$=CH_3{\cdot}CH_2{\cdot}COOH+2CH_3{\cdot}COOH+2CO_2.$$

Succinic acid has been found in this fermentation, and has been attributed to the reductive deamination of aspartic acid present in the medium (van Niel, Dissert. Delft, 1928); it has now been shown that it occurs in the fermentation of glycerol when no aspartic acid is present and when its origin from the former compound is therefore certain. It has also been shown that CO_2 added to the fermentation is utilised and the succinic acid thereby increased, 1 mol. CO_2 absorbed giving rise to 1 mol. succinic acid (Wood and Werkman, Biochem. J. 1938, **32**, 1262).

Glycerol is fermented almost quantitatively to propionic acid; the course of this reaction is not clear, but is explicable on the assumption that glycerol is first oxidised to triose, which is then reduced by another molecule of glycerol to propionic acid. The primary hydrogen acceptor necessary for the preliminary oxidation of glycerol is present in the yeast water or peptone in which the fermentation is usually carried out (van Niel, *l.c.*).

Using washed suspensions of bacteria, Virtanen and Karström (Acta. Chem. Fennica, B. 1931, **7**, 17) showed that glucose was decomposed to propionic and acetic acids, carbon dioxide and succinic acid. Dried bacteria in presence of toluene gave hexosemonophosphate, acetic and succinic acids. On these results a scheme was put forward by which the breakdown of hexose by untreated bacteria gives hexosemonophosphate, which is decomposed to an unidentified 3-carbon compound and thence to propionic and acetic acids and carbon dioxide. In dried preparations of bacteria with toluene, hexosemonophosphate is not further broken down. According to these workers, succinic acid is produced both by untreated and by dry toluene treated organisms by an alternative type of hexose breakdown into 2- and 4-carbon compounds; these finally appear as acetic and succinic acids (*see* origin of succinic acid, *below*).

Evidence that propionic fermentation may occur, through a phosphorylation cycle analogous to the Embden-Meyerhof-Parnas cycle for yeast, has been obtained by Stone and Werkman (Biochem. J. 1937, **31**, 1516), who isolated phosphoglyceric acid from the fermentation of glucose in the presence of fluoride by three different strains of propionic bacteria.

It is clear that no convincing evidence in favour of any course of hexose breakdown in this fermentation has so far been adduced, through certain possibilities have been indicated.

Fermentation by the Bacteriaceæ (*coli-typhosus group*).—The products of fermentation by this group of organisms are so numerous that no product predominates sufficiently to give its name to the fermentation. Harden (J.C.S. 1901, **79**, 610), was the first to construct a picture of the breakdown process as a whole; this he did by estimating each product and deducing how the carbon of the original hexose molecule was partitioned among the products of fermentation. The products of the fermentation of glucose by *Bact. coli* found by Harden were lactic and acetic acid, alcohol, succinic acid, carbon dioxide, formic acid and hydrogen. From his quantitative results, he represented the final equilibrium as follows:

$$2C_6H_{12}O_6+H_2O=2CH_3{\cdot}CH(OH)COOH$$
$$+CH_3{\cdot}COOH+C_2H_5{\cdot}OH+2CO_2+2H_2.$$

Fructose, galactose and arabinose gave the same products in about the same proportions as glucose, mannitol gave more ethyl alcohol and less acetic and lactic acids, whilst later Kay (Biochem. J. 1926, **20**, 321) showed that more oxidised substrates, gluconic, glycuronic and saccharic acids give more acetic and succinic acids and less ethyl alcohol. Scheffer (Dissert. Delft. 1928) and Kluyver (*op. cit.*) further elaborated these quantitative results, studying the fermentation of glucose in peptone or yeast water by growing cultures of various members of the *Bacteriaceæ* and accounting quantitatively in the end products obtained for the sugar fermented. Scheffer interpreted his results in accordance with the Neuberg scheme of fermentation then generally accepted, though he believed the primary split of the hexose molecule to occur *via* a phosphorylation. The scheme advanced for this breakdown is contained in Fig. 1. According to this scheme, the primary cleavage of the hexose molecule is supposed to give rise to methylglyoxal hydrate, the decomposition of which occurs in two ways: (1) to lactic acid, and (2) to acetaldehyde and formic acid; the latter decomposes to CO_2 and H_2 (discussed on p. 44), whilst the former gives rise by a dismutation to acetic acid and ethyl alcohol. The evidence for this series of reactions is briefly as follows:

(1) Methylglyoxal when acted on by washed suspensions of this organism gives rise to lactic acid quantitatively (Neuberg and Gorr, Biochem. Z. 1925, **162**, 490).

(2) Acetic acid and ethyl alcohol (as first noted by Harden) occur in approximately equimolecular ratios and hence a common precursor may be postulated (Harden, J.C.S. 1901, **79**, 610).

(3) Acetaldehyde has been obtained from this fermentation by the use of sulphite (Neuberg and Nord, Biochem. Z. 1919, **96**, 133).

(4) Methylglyoxal has been obtained by the action of dried *Bact. coli* on magnesium hexosephosphate in toluene-water (Fromageot, *ibid.* 1929, **216**, 467).

In the case of mannitol a preliminary oxidation is required before the first reaction can occur; once the fermentation has started the hydrogen acceptor may be acetaldehyde, the reduction of which provides the extra ethyl alcohol noted; gluconic, glycuronic and saccharic acids must be reduced before they can pass to triose and this reduction accounts for

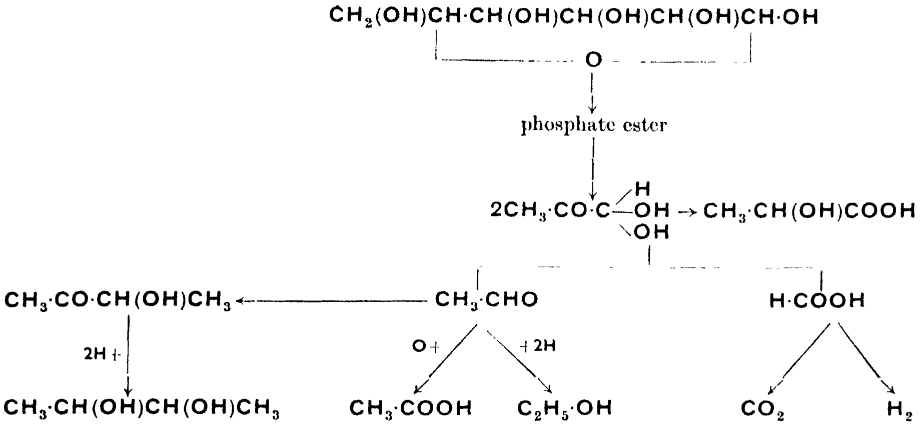


FIG. 1.

the extra acetic acid found in these fermentations. The production of acetylmethylcarbinol (acetoin) and 2:3-butylene glycol (Harden and Walpole, Proc. Roy. Soc. B, 1906, **77**, 399) occurs in all those members of the *Bacteriaceæ* giving the Voges-Proskauer reaction (Harden, *ibid.* 424; Harden and Norris, J. Physiol. 1911, **42**, 332). Acetoin probably occurs from the enzymic condensation of 2 mol. of acetaldehyde as shown by Neuberg and Hirsch in the case of yeast (Biochem. Z. 1921, **115**, 282); once formed, it may be reduced to 2:3-butylene glycol.

Succinic acid is not provided for in the scheme given in Fig. 1; Harden (J.C.S. 1901, **79**, 610) originally suggested that it occurred through the oxidative condensation of 2 mol. of acetic acid, but no corroborative evidence has been obtained. Virtanen (Acta Soc. Sci. Fennicæ, Comment. Physico-Math. 1925, **2**, 20; J. Bact. 1934, **28**, 447) suggested that succinic acid does not take its origin along the lines given in Fig. 1, but that a second type of hexose cleavage occurs into a C_2 and a C_4 compound, a final rearrangement occurring so as to give acetic acid, ethyl alcohol and succinic acid (Fig. 2); further evidence for this view is given by Scheffer (*op. cit.*). Evidence that succinic acid may arise by another route is contained in the observation that its production in the fermentations of glucose, galactose and pyruvic acid by *Bact. coli* is strongly influenced by the CO_2 present (Elsden, Biochem. J. 1938, **32**, 187); for example, the rate of succinic acid formation from glucose can be increased about 400% on passing from an atmosphere of pure nitrogen to 5% CO_2 in nitrogen. This observation fits in with those recorded in the propionic fermentation (p. 42).

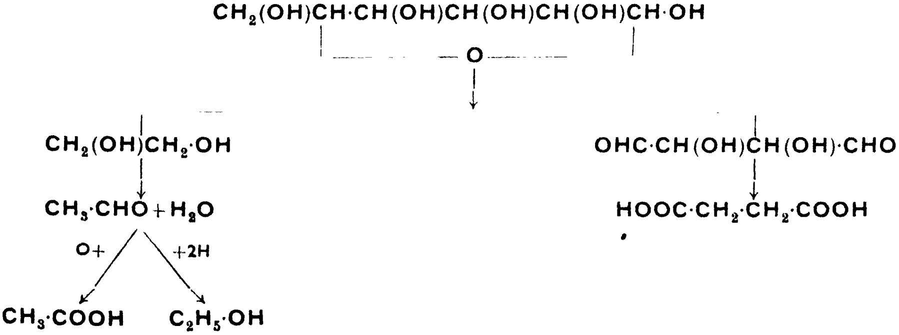


FIG. 2.

Evidence exists that fermentations by the *Bacteriaceæ* may go through a phosphorylation cycle. Tikka (Biochem. Z., 1935, **279**, 264) has shown that, using a dried preparation of *Bact. coli*, an esterification of glucose and phosphate occurs, whilst Stone and Werkman (*l.c.*) have isolated phosphoglyceric acid by the action of washed suspensions of *Bact. coli* and *Aerobacter indologenes* on glucose in the presence of phosphate buffer, $MgCl_2$, acetaldehyde and toluene. Hexose-diphosphate and glucose are fermented by *Bact. coli* to give the same fermentation products, and both fermentations are influenced in the same way by changes in p_H. In the absence of inhibitors phosphoglyceric acid is decomposed to acetic and formic acids, whilst glycerolphosphate gives ethyl alcohol and formic acid (78% yield). Phosphoglyceric acid in the presence of toluene gives pyruvic and phosphoric acids (72·8% yield), whilst pyruvic acid gives acetic, formic and lactic acids. There is thus some evidence, very far from conclusive, that the fermentation of glucose by *Bact. coli* may proceed according to Fig. 3; the substances in brackets have not been isolated, and the reactions indicated by the dotted lines have not been proved to occur.

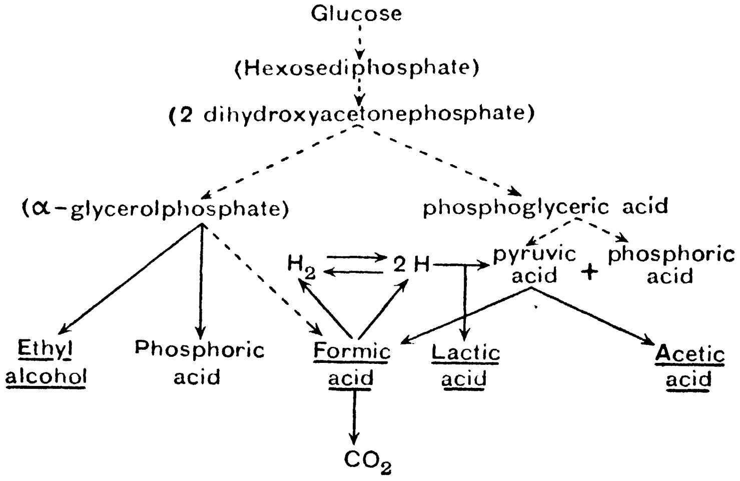


FIG. 3.

THE PRODUCTION OF MOLECULAR HYDROGEN.—The first observation of free hydrogen in fermentation was from calcium formate by mixed cultures from mud (Popoff, Pflügers Archiv, 1875, **10**, 113), followed by the demonstration that the calcium formate was decomposed as follows:

$$(COOH)_2Ca + H_2O = CaCO_3 + CO_2 + 2H_2$$

(Hoppe-Seyler, Pflügers Archiv, 1876, **12**, 1.) Frankland *et al.* showed the production of hydrogen for the first time by pure cultures (J.C.S. 1892, **61**, 254, 432, 737) from mannitol, dulcitol, glucose and arabinose. In 1901 Pakes and Jollyman (*ibid.* 1901, **79**, 386), working with pure strains of a number of "gas producing" bacteria, showed that those organisms which produced hydrogen from glucose decomposed formate into equimolecular proportions of hydrogen and carbon dioxide; they deduced that the gas from glucose comes *via* formate. These observations were confirmed by Harden (1901, *l.c.*). The liberation of free hydrogen from formate has been shown to be due to an enzyme (*formic hydrogenlyase*) catalysing the reaction $H{\cdot}COOH \rightleftharpoons H_2 + CO_2$ (Stephenson and Stickland, Biochem. J. 1932, **36**, 712). The reversibility of this reaction has been shown by Woods (*ibid.* 1936, **30**, 515). This enzyme is distinct from *formic dehydrogenase* catalysing the reaction $H{\cdot}COOH + X = XH_2 + CO_2$, where X is any hydrogen acceptor, and also from a combination of this enzyme with hydrogenase catalysing the reaction $H_2 + X = XH_2$. Proof of this will be found in the literature cited (*see also* Stephenson, Ergbn. Enzymforsch. 1937, **6**, 139). Formic hydrogenlyase is an adaptive enzyme depending for its formation on growth conditions. In highly aerobic conditions in the absence of carbohydrate or formate it is absent or at a minimum, and is most active in organisms grown anærobically in presence of formate (Yudkin, Biochem. J. 1932, **26**, 1859; Stephenson, *l.c.*). So far it appears that free hydrogen is produced from sugars only *via* formate. Stephenson and Stickland (1932, *l.c.*) adduced evidence that in the case of *Bact. coli* it could be produced from glucose by another mechanism; this view has been challenged and discussed fully (Stephenson, Ergbn. Enzymforsch. *l.c.*). As far as the *Bacteriaceæ* are concerned, it cannot be regarded as settled. More recently, however, it has been shown that *Cl. tetanomorphum* produces hydrogen from glucose and pyruvate but not from formate (Woods and Clifton, Biochem. J. 1937, **31**, 1774), and *Cl. Welchii* from glucose but not from formate (Woods, unpublished). Thus formate is not the sole substrate for the production of free hydrogen in organisms of other groups.

THE FERMENTATION OF GLYCEROL.—A detailed study of the fermentation of glycerol by members of the *Bacteriaceæ* was made by Braak (Dissert. Delft. 1928). The products obtained were qualitatively the same as from glucose (Scheffer, *op. cit.*), but the proportion of reduced products higher. In the case of *Bact. lactis ærogenes*, acetoin and 2:3-butylene glycol appear only in traces. With most members of the group the initial attack on glycerol requires the presence of a hydrogen acceptor to oxidise glycerol to a triose; in broth and peptone media this is frequently provided by aspartic acid, which is deaminated to succinic acid; unless a hydrogen acceptor is present in sufficient quantity, the fermentation comes to a standstill before it is complete. One member of the group, however (*Bact. freundii*), was isolated, which is capable of dispensing with an added hydrogen acceptor, being able to effect a dismutation of glycerol to triose and trimethylene glycol (Braak, *l.c.*):

$$2CH_2(OH)CH(OH)CH_2{\cdot}OH = CH_2(OH)CH_2{\cdot}CH_2{\cdot}OH + C_3H_6O_3 + H_2O.$$

BUTYRIC FERMENTATION AND ACETONE PRODUCTION.—The bacterial production of butyric acid from carbohydrate was shown by Pasteur in 1861, and is historically interesting as furnishing the material for his observations on strict anærobes. The actual chemistry of butyric fermentation was first studied by Fitz (Ber. 1876, **9**, 1348), who isolated an organism decomposing glycerol with the production, as the main products, of *n*-butyl alcohol and *n*-butyric acid, which were also obtained from mannitol, starch and invert sugar. The discovery of this fermentation was the first example of the production of a 4-carbon from a 3-carbon compound, and Fitz himself suggests that the production of the former occurs by a condensation of two 2-carbon compounds in a manner analogous to aldol condensation. The isolation of acetaldehyde in a butyric fermentation by the use of sulphite (Neuberg and Arinstein, Biochem. Z. 1921, **117**, 269) and the simultaneous disappearance of 4-carbon compounds supported the idea of the production of the latter by aldol condensation. The fermentation of pyruvic acid by *B. butylicus*, however, led to no 4-carbon products, but only to acetic and formic acids (Neuberg and Arinstein, *l.c.*). Nevertheless the occurrence of butyl products by aldol condensation continued to find support (van der Lek, Dissert. Delft, 1930; Kluyver, *op. cit.*). Actually the addition of acetaldehyde to a butyl alcohol acetone fermentation by *Cl. butylicum* gave a 60% increase in the yields of butyl alcohol, whilst added acetaldol was unchanged (Bernhauer and Kürschner, Biochem. Z. 1935, **280**, 379); furthermore, propionaldehyde is reduced to propyl alcohol, giving no condensation product. Aldol condensation as a step in the production of 4-carbon compounds therefore is not proved.

The production of 4-carbon compounds is often accompanied by acetone. Schardinger (Zentr. Bakt. II, 1905, **14**, 772) first isolated an organism producing acetone with formic and acetic acids and ethyl alcohol from starch. Other workers later used organisms producing acetone, ethyl and butyl alcohols, butyric, acetic and formic acids, carbon dioxide and hydrogen (Fernbach and Strange, 1912, B.P. 21073; Weizmann, B.P. 1915, 4845; Reilly *et al.* Biochem. J. 1920, **14**, 229). The early stages of the fermentation are characterised by a high acid production followed by a fall accompanied by a rise in the production of gaseous products, butyl alcohol and acetone (Reilly *et al.*, *ibid.* 1920, **14**, 229; Osburn *et al.*, J. Biol. Chem. 1937, **121**, 685). Speakman (*ibid.* 1920, **41**, 319) using *Granulobacter pectinovorum* showed that the addition of acetic acid to the fermenting mash increased the production of acetone by 45%; evidence that acetic acid is a direct precursor of acetone is, however, shaken by the fact that other acids, *e.g.* propionic acid and butyric acid in similar concentrations increase acetone production by 30% and 10% respectively. More recent work shows the effect of p_H on the final products. In the early stages of the fermentation of glucose by *Cl. butylicum* butyric and acetic acids predominate, butyl and *iso*propyl alcohols and acetone occur later. If the p_H is maintained above 6·7 by addition at intervals of $NaHCO_3$ the formation of alcohols is largely suppressed and that of the acids increased; formic and lactic acids also appear. Pyruvic acid and methylglyoxal have been isolated as intermediates (Osburn *et al.*, *ibid.* 1937, **121**, 685). The addition of certain products during the course of the fermentation furnishes evidence of intermediate processes, thus butyric and acetic acids increase butyl and *iso*propyl alcohols, $CH_3{\cdot}CHO$ gives rise to $C_2H_5{\cdot}OH$ and traces of acetylmethylcarbinol and 2:3-butylene glycol; acetone and acetoacetic acid both increase *iso*propyl alcohol (Osburn *et al.*, Iowa State Coll. J. of Science, 1938, **12**, 275).

A BACTERIAL ALCOHOLIC FERMENTATION.—An organism isolated from agave juice ferments glucose, fructose and mannose to ethyl alcohol and carbon dioxide in equimolecular proportions; small amounts of lactic acid are also found (Kluyver and Hoppenbrouwers, Arch. Mikrobiol. 1931, **2**, 245).

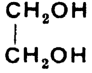
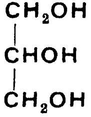
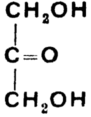
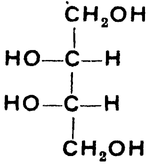
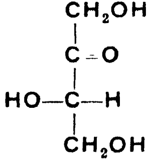
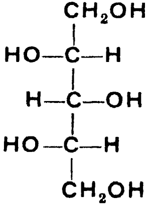
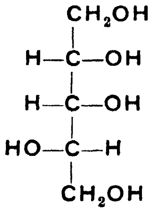
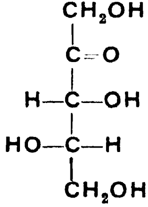
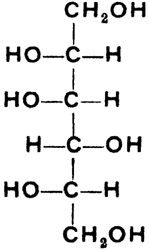
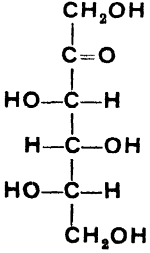
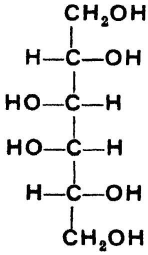
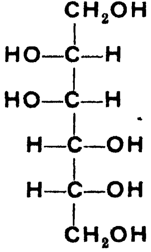
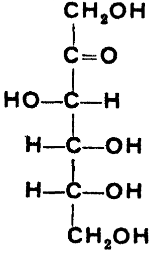
THE DISLOCATION OF FERMENTATIONS.—It is becoming apparent that the course of fermentations and the proportions of various products obtained can be influenced by adjusting conditions. This is implicit in some of the observations already recorded, but other striking instances may be given. Thus the fermentation by *Bact. coli* can be so altered as to become predominantly a lactic fermentation (72–98% lactic acid); this has been done by using hexosediphosphate as substrate and adding toluene and glutathione. These conditions favour the production of methylglyoxal and the action of glyoxalase (for which glutathione is the coenzyme), and lactic acid is therefore produced at a rate greatly exceeding that in usual conditions of fermentations (Cattaneo and Neuberg, Biochem. Z. 1934, **272**, 441). In the case of *Cl. butyricum* the normal fermentation in argon (probably also in nitrogen) accords with the equation:

$$C_6H_{12}O_6 = C_4H_8O_2 + 2CO_2 + 2H_2.$$

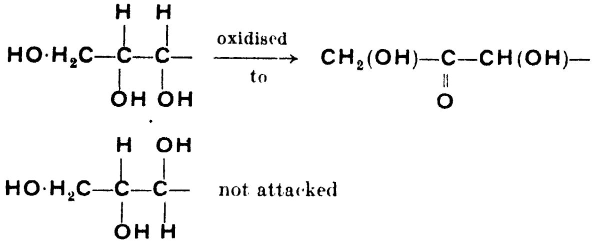
The production of butyric acid is inhibited by carbon monoxide, the inhibition being reversible by light of high intensity; it is also inhibited by cyanide, $M/1{,}000$ and $M/100$ to the extent of 60% and 100% respectively. These inhibitions do not, however, prevent the primary disruption of the hexose molecule, but only the subsequent reactions by which carbon dioxide, hydrogen and butyric acid are produced, the whole of the sugar now appearing as lactic acid. Thus in carbon monoxide alone a pure lactic fermentation occurs, in pure argon a pure butyric fermentation (as in equation above) takes place, while in argon+5–25% carbon monoxide, mixed lactic and butyric fermentations are obtained (Kempner, *ibid.* 1933, **257**, 41; Kempner and Kubowitz, *ibid.* 1933, **265**, 245; Kubowitz, *ibid.*, 1934, **274**, 285).

Fermentations Involving Partial Oxidation (the Acetic Fermentations).—The production of vinegar from alcohol residues is an ancient biochemical industry, the bacterial agent for which was demonstrated by Pasteur in 1862–64 (Pasteur, "Oeuvres," III, Masson et Cie.). This oxidation is, however, only one among many of which acetic bacteria are capable. Thus it was early shown that *B. aceti* and *B. xylinum* oxidise propyl alcohol and glycol to propionic and glycolic acids respectively, glucose to gluconic acid and mannitol to fructose (Brown, J.C.S. 1887, **51**, 638). These reactions exemplify the oxidation of primary alcohols and aldehydes to carboxylic acids and secondary alcohols to ketones. By the classical work of

TABLE I.

Not attacked.	Attacked.	Product.
Ethylene Glycol. 	Glycerol. 	Dihydroxyacetone. 
	i-Erythritol. 	*l*(+) Erythrulose. 
i-Xylitol. 	Arabitol. 	" Arabinulose " (araboketose) 
	l(−)-Sorbitol. 	*l*(−)-Sorbose. 
i-Dulcitol. 	*d*(−)-Mannitol. 	*d*(−)-Fructose. 

Bertrand (Ann. Chim. Phys. 1904, [viii], **3**, 181), it was shown that the sorbose bacillus (now known as *B. xylinum*) oxidises only those secondary alcohols with two adjacent *cis*-OH groups.



$$HO{\cdot}H_2C-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}- \xrightarrow[\text{to}]{\text{oxidised}} CH_2(OH)-\underset{O}{\overset{\|}{C}}-CH(OH)-$$

$$HO{\cdot}H_2C-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}- \quad \text{not attacked}$$

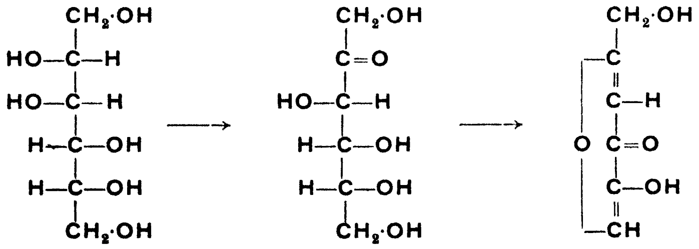
This is made clear by Table I on the opposite page.

Hermann and Neuschul divided the whole group of acetic bacteria into the ketogenic and aketogenic classes. From Table II it is clear that, while the oxidation of aldehydes to acids is brought about by most members of the group, the oxidation of secondary alcohols to ketones is more restricted (Biochem. Z. 1931, **233**, 129).

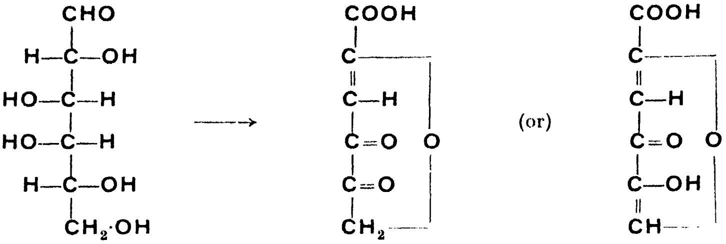
Table II.—Oxidations Catalysed by Acetic Bacteria (Hermann and Neuschul).

	Glucose to gluconic acid.	Arabinose to arabonic acid.	Galactose to galactonic acid.	Fructose to ketogluconic acid.	Glycerol to dihydroxyacetone.	Erythritol to erythrulose.	Mannitol to fructose.	Sorbitol to sorbose.	Dulcitol to galactose.	Gluconic acid to 5-ketogluconic acid.
Ketogenic										
B. gluconicum	+	+	+	+	+	+	+	+	+	+
B. xylinum	+	+	+	0	+	+	+	+	0	+
B. xylinoides	+	+	+	0	+	+	+	+	0	+
B. orleanense	+	+	+	0	+	+	+	+	0	+
B. aceti (Hansen)	+	+	+	0	+	+	+	0	0	+
Aketogenic										
B. aceti (Henneberg)	+	0	0	0	0	0	+	0	0	+
B. pasteurianum	+	+	+	0	0	0	0	0	0	0
B. acetosum	+	+	+	0	0	0	0	0	0	0
B. rancens	+	+	+	0	0	0	0	0	0	+
B. ascendens	+	+	+	0	0	0	0	0	0	0
B. vini acetati	+	+	+	0	0	0	0	0	0	0
B. kützingianum	+	0	0	0	0	0	0	0	0	0
B. ascendens (Henneberg)	0	+	+	0	0	0	0	0	0	0

Certain species of acetic bacteria isolated in Japan produce kojic acid in small yield from fructose and mannitol, and comenic acid from galactose (Takahashi and Asai, Zentr. Bakt. II, 1933, **88**, 286; *ibid.* 1936, **93**, 248).



Mannitol. Fructose. Kojic acid.



Galactose. Comenic acid.

Considerable controversy has arisen as to the actual enzymic process by which acetic acid is formed. Acetaldehyde has been shown to occur as an intermediate in the oxidation of ethyl alcohol (Neuberg and Nord, Biochem. Z. 1919, **96**, 175); the fate of the acetaldehyde may be either *via* a dismutation to ethyl alcohol and acetic acid followed by an oxidation of the ethyl alcohol as before, or the acetaldehyde may be oxidised direct to acetic acid. Dismutation has been shown to occur (Neuberg and Windisch, *ibid.* 1925, **166**, 455), but at the acid reaction prevailing in the vinegar process it proceeds extremely slowly as compared with oxidation (Wieland and Bertho, Annalen, 1928, **467**, 95; Janke and Kropacsy, Biochem. Z. 1935, **278**, 37). The commercial production of acetic acid must therefore be regarded as mainly due to an oxidation of acetaldehyde.

The dismutation of other aldehydes to their corresponding alcohols and acids also occurs (Molinari, *ibid.* 1929, **216**, 187), viz. propaldehyde, furfural, *n*-butaldehyde, *iso*-valeraldehyde, citronellal, cinnamaldehyde and anisaldehyde.

For further details respecting acetic fermentations, *see* Butlin, "The Chemical Activities of the Acetic Bacteria," Chemistry Research Special Report, No. 2, 1936, H.M. Stationery Office; Bernhauer, Ergbn. Enzymforsch. 1938, **7**, 246.

M. S.

FERMENTATION, MOULD. INTRODUCTION.—The study of the biochemistry of the lower fungi (moulds) received considerable impetus from the classical researches of Carl Wehmer, carried out in the last decade of the nineteenth century. Wehmer demonstrated clearly that moulds were able to produce from sugar large amounts of organic acids, such as oxalic and citric acid, by a true fermentation process which ranked with the fermentations due to yeasts and bacteria. Prior to Wehmer's researches the general impression with regard to mould activity was that these organisms were agents in the transformation of organic matter into carbon dioxide and water, with almost complete absence of isolable intermediate products.

Biochemical Characteristics of Moulds as compared with Yeasts and Bacteria.—Moulds are multicellular organisms and show a type of vegetation entirely different from that characteristic of the unicellular organisms such as yeasts and bacteria. Further, they are strictly aerobic in nature and therefore grow on liquid or solid media as a surface film. This type of growth offers facilities for access of atmospheric oxygen denied to organisms distributed throughout a liquid medium, and it would be expected that in general mould products would tend to be more highly oxidised than those of the unicellular organisms. Such is undoubtedly the case and accounts for the production in high yield of various carboxylic acids which are at a higher level of oxidation than the nutrient (sugar) supplied. Analogies are to be found in this respect with some of the oxidising bacteria.

The production of typical plant acids by moulds suggests affinities with the higher plants. It must be emphasised, however, that moulds differ from all the green plants in possessing no chlorophyll. They are therefore incapable of assimilating atmospheric carbon dioxide by means of the energy derived from sunlight and of building it up into organic molecules. The energy of moulds must therefore be derived from the organic substrates on which they grow. They are dependent on organic carbon both for energy and as a source of the cell substances and other metabolic products formed. In most of the work here reported the carbon is supplied as sugar—usually glucose.

In spite of their aerobic method of growth some moulds produce alcoholic fermentations and thus resemble the yeasts. Outstanding in this respect is the genus *Fusarium*, all species of which seem to produce alcohol in yields comparable with those obtained in an ordinary alcoholic fermentation by yeast. Other substances which are formed as by-products in yeast fermentation such as glycerol, acetaldehyde and succinic acid are also produced by moulds.

In alcoholic fermentation external oxygen does not enter into the reaction. The main product, apart from carbon dioxide, is of course ethyl alcohol, which is at a lower stage of oxidation than the sugar supplied. Moulds are capable of other types of fermentation in which the product is at a lower oxidation level than the substrate. A typical example is the production of mannitol which is formed in high yield by several mould species.

Moulds thus possess certain affinities with both yeasts and bacteria. They have, however, one outstanding biochemical characteristic differentiating them from the unicellular organisms. They have the power of building up from the six-carbon chain of a hexose a large number of complex crystalline products, many having more than six carbon atoms, and including representatives of a wide variety of organic compounds.

It is surmised that the synthetic powers shown by the lower fungi may be in part due to their capability of producing substances on a higher, lower or the same level of oxidation as the starting material (sugar). Bearing in mind the fact that moulds are at the same time rich in enzymes of every type, including hydrolytic enzymes, and that the action of these enzymes is probably reversible under suitable conditions, it is readily seen that all the essentials are present for a wide variety of syntheses as well as degradations.

Metabolic Products.

PRODUCTION OF ORGANIC ACIDS.

It is convenient to consider first the production of oxalic, citric and gluconic acids since not only are they of considerable historical and industrial importance, but they also illustrate the oxidising capabilities of moulds, as they are all products at a higher stage of oxidation than the starting material (sugar).

Oxalic Acid.—Although several observers had reported the presence of calcium oxalate crystals in cultures of various fungi, the proof that oxalic acid in the free state is produced by fungi, especially by *Aspergillus niger*, solely in the presence of carbohydrates or chemically allied substances was afforded by Wehmer (Bot.-Ztg. 1891, **49**, 233 ; Ber. deut. bot. Ges. 1891, **9**, 163). He made a study of the conditions of oxalic acid production, with the result that the process was definitely ranked with other fermentations produced by micro-organisms.

The acidity of the metabolism solution slowly rises to a maximum as the mould develops and begins to decline when all the sugar is exhausted. Lower temperatures than the optimum for growth favour the accumulation of acid. If calcium carbonate is added to the metabolism solution to combine with the acid, the accumulation of the combined acid is progressive and the resulting calcium oxalate may amount to more than 100% of the sugar originally present, the yield of oxalic acid on sugar being about 50% of theoretical. Other moulds, notably *Penicillium oxalicum* (Currie and Thom, J. Biol. Chem. 1915, **22**, 287), have been shown to produce oxalic acid.

Citric Acid.—For the manufacture of citric acid by Mould Fermentation *v.* CITRIC ACID (Vol. III, pp. 188, 189).

Mechanism of Citric Acid Formation.—The conversion of the straight chain of six carbon atoms of a hexose to the branched chain of citric acid by the agency of micro-organisms has evoked considerable interest, and a number of hypotheses have been advanced to account for the mechanism of this reaction, without, however, reaching any finality.

Some of these hypotheses can be eliminated by a consideration of the yields attainable. Thus a preliminary breakdown of hexose similar to that encountered in alcoholic fermentation by yeast can play no part in the formation of citric acid by moulds. For the theory of Bernhauer (Ergebn. Enzymforsch. 1934, **3**, 185) to hold, the weight ratio of citric acid to carbon dioxide should not exceed 1·45:1 and the weight yield of citric acid from glucose should not exceed 71·1%, but ratios up to 4:1 and yields up to 90% were actually obtained by Wells *et al.* (J. Amer. Chem. Soc. 1936, **58**, 555). Similarly Emde's hypothesis in which quinic acid is an intermediate (Biochem. Z. 1935, **275**, 373) is excluded since the maximum yield of citric acid from sucrose would be only 56%, and correspondingly less from a hexose. In view of the lack of success in obtaining conclusive evidence as to the mechanism of the citric acid fermentation, in which the conditions have been extensively studied, it is not surprising that little attention has been devoted to the mechanism of formation of other mould products, which are at present of purely academic interest in most cases.

***d*-Gluconic Acid.**—The production of gluconic acid as a fermentation product of the lower fungi was first observed by Molliard (Compt. rend. 1922, **174**, 881). He found that the acid is produced in considerable yield from sucrose by *Aspergillus niger.* It has since been isolated from the products of metabolism of a number of other species such as *Aspergillus fuscus, cinnamomeus* and *oryzæ* ; *Penicillium glaucum, purpurogenum, chrysogenum, crustaceum* and *Fumago vagans.* In all cases it seems to be formed from glucose or a polysaccharide which yields glucose on hydrolysis, by a simple oxidation of the aldehyde group of the sugar to a carboxyl group, without the intervention of a complicated series of changes such as evidently occur in the formation of citric acid. Evidence for this is the preparation by Müller (Biochem. Z. 1928, **199**, 136; 1929, **205**, 111) of an oxidising enzyme from the press juices of *Aspergilli* and *Penicillia* capable of converting glucose to gluconic acid. This enzyme was termed by Müller "glucose-oxidase." The evidence is further supported by a discovery of Angeletti and Cerruti (Annali Chim. Appl. 1930, **20**, 424) that one of the organisms responsible for gluconic acid production, namely *P. purpurogenum* var. *rubrisclerotium* is able to convert mannose into *d*-mannonic acid.

As gluconic acid is of some commercial importance, the possibilities of its industrial production by mould fermentation have been studied by May *et al.* (Ind. Eng. Chem. 1929, **21**, 1198, *cf.* May *et al.*, J. Biol. Chem. 1927, **75**, 77; Herrick and May, *ibid.* 1928, **77**, 185). They employed as their organism *P. purpurogenum* var. *rubri-sclerotium.* This was cultivated on a semi-large scale plant in shallow aluminium pans. Using a 20% solution of commercial glucose they were able to obtain yields of about 57% of theoretical. The acid was recovered as the calcium salt, which is readily purified by recrystallisation from water. The mould *P. chrysogenum* was later found to be more satisfactory for the reaction and the process was further improved by using submerged growths under increased air pressure and agitation in sintered-bottom washing bottles. The most promising results were obtained with a selected strain of *Aspergillus niger.* A rotary aluminium drum was used as the fermentation vessel and a regulated air supply was introduced under pressure. This method represents an important departure from the shallow pan method of cultivation hitherto employed with moulds, bringing the process more into line with vat fermentations, such as are used for yeasts and bacteria. This results in a considerable saving of plant space.

The most efficient glucose concentration for the reaction was found to be 15–20% and the acid was neutralised by adding 26 g. of calcium carbonate per litre of culture solution. Fermentations could be made with germinated or ungerminated spores, the latter requiring a somewhat longer time, and the same mycelial growth could be used for successive fermentations. Under the best conditions with 15% glucose solutions yields of gluconic acid in excess of 95%, based on the sugar present, were obtained in a 24-hour fermentation period. The apparatus and conditions employed on the pilot plant scale, in which the drum has a capacity of 420 gallons, the optimum charge being 175 gallons, are described by Gastrock *et al.* (Ind. Eng. Chem. 1938, **30**, 783).

The acids oxalic, citric and gluconic acid are thus all products of the metabolism of one organism, *Aspergillus niger*, although they can all be obtained, at any rate, singly from other moulds. The predominance of one or other of these acids in the metabolism solution is largely a function of the inorganic nutrient. By a correct choice of the source and amount of nitrogen and other essential elements in the medium the metabolism can be directed so as to obtain the desired product. Much work has been devoted to a study of the conditions for obtaining the best yields of each of these acids, particularly citric and gluconic acid. For an account of this work on the effect of nutrients the literature should be consulted.

Other simple organic acids produced by mould fermentation will now be briefly reviewed.

Fumaric Acid.—The formation of fumaric acid by micro-organisms was first observed in 1911 by Ehrlich (Ber. 1911, **44**, 3737), who isolated it from the metabolic products of *Mucor stolonifer* when grown on glucose and fructose solutions. Wehmer (1918) described a strain of *Aspergillus* akin to *A. niger*, which produced fumaric acid from sucrose in 60–70% yield. He named the mould *A. fumaricus*, but observed that it gradually lost completely its power to produce fumaric acid. On the other hand, considerable amounts of gluconic acid, with varying amounts of citric and some malic acid, were produced (Biochem. Z. 1928, **197**, 418). Thies (Zentr. Bakt. II, 1930, **82**, 321), by adopting special conditions of culture, was able to obtain a heavy submerged growth with the production of appreciable amounts of fumaric acid. Takahashi and Asai (Proc. Imp. Acad. Tokyo, 1927, **3**, 85) found that fumaric acid was produced in small amount by *Rhizopus* species, and Gottschalk (Z. physiol. Chem. 1926, **152**, 136) obtained it from pyruvic acid by the agency of *R. nigricans*. It is also formed in small amount by a *Penicillium* species (Raistrick and Simonart, Biochem. J. 1933, **27**, 628).

Succinic Acid.—Succinic acid has been recorded as being formed in small amount by a number of moulds. It was obtained by Fitz (Ber. 1873, **6**, 48) from *Mucor mucedo*, and by Emmerling from *M. racemosus*. Takahashi and Asai isolated it from the products of several species of *Mucor* grown on glucose in presence of calcium carbonate. It has also been obtained from other genera, notably *Aspergillus*, *Clasterosporium*, *Fumago* and *Penicillium*.

Malic Acid.—Small amounts of malic acid have been found in the fermentation products of several of the lower fungi. Thus Wehmer (*l.c.*) showed that it is formed from sucrose by *Aspergillus fumaricus*. Birkinshaw *et al.* (Phil. Trans. 1931, B, **220**, 153) obtained it from a white *Aspergillus*, and Birkinshaw and Raistrick (Phil. Trans. 1931, B, **220**, 331) from a *Clasterosporium* species when grown on glucose. Yuill (Chem. and Ind. 1936, **55**, 155) found that it was formed in fair quantity by a sub-surface fermentation of *A. flavus* Link, in presence of chalk. Under these conditions succinic and fumaric acids are also obtained.

Since the acids succinic, fumaric and malic acid are closely related chemically and are interconvertible by means of enzymes, it seems likely that they all arise by the same general reaction from sugar, and not by deamination of amino acids derived from breakdown of cell proteins, as has been postulated for the production of succinic acid by yeast fermentation. This latter origin would seem to be excluded in the case of fumaric acid at any rate since it has been obtained in large yield, and may be regarded as a major product of fermentation.

Formic Acid.—Formic acid is a product of fermentation of arabinose by *A. oryzæ* (Takodoro, J. Agric. Chem. Soc. Japan, 1935, **11**, 365), other products being citric and *glycollic acid*, with smaller amounts of oxalic and kojic acids and glyceraldehyde. From fucose, formic, glycollic and lactic acids are produced.

Pyruvic Acid.—This acid is obtained along with *dimethylpyruvic acid* by the growth of *A. niger* on glucose or sucrose in the presence of sodium sulphite (Hida, J. Shanghai Sci. Inst. 1935, [iv], **1**, 201). The presence of ammonium salts in the medium inhibits the production of pyruvic and increases that of dimethylpyruvic acid.

Itaconic Acid.—Kinoshita (Acta Phytochim. 1931, **5**, 271), observed the production of itaconic acid together with gluconic and citric acids from sucrose or fructose, but not from glucose, by the agency of a mould which he named *Aspergillus itaconicus*, derived from the juice of pickled plums. Kinoshita suggests that the sequence of formation of products is sugar → gluconic acid → citric acid → aconitic acid → itaconic acid. *Aconitic acid* has been obtained from citric acid using a strain of *A. niger* which was also able to accomplish the reverse transformation (Bernhauer and Böckl, Biochem. Z. 1932, **253**, 16, 25). Recently Calam *et al.* have identified itaconic acid as a metabolic product of *A. terreus* Thom (Biochem. J. 1939, **33**, 1488), but found no evidence that citric acid represents an intermediate stage in its formation.

Lactic Acid.—Lactic acid differs from the preceding acids in that it represents a product of rearrangement (and fission) of the hexose molecule, but is not an oxidation product of the sugar.

Although lactic acid has frequently been reported as a metabolic product of bacteria, it is not of frequent occurrence amongst mould products. Most of the recorded observations relate to the genus *Rhizopus*, where, however, it has been encountered in high yield. Thus Kanel (Microbiol. U.S.S.R. 1934, **3**, 259) obtained from a species allied to *R. japonicus* a 40% yield of lactic acid from sugar on a medium containing chalk. Ward *et al.* (J. Amer. Chem. Soc. 1936, **58**, 1286) obtained reproducible yields of 19–62% of lactic acid from glucose on a medium containing calcium carbonate using *R. oryzæ*, *arrhizus* and *tritici*. Two species of *Rhizopus* isolated by Waksman and Hutchings (J. Amer. Chem. Soc. 1937, **59**, 545) from soil and from composts of decomposing organic matter produced 60–70% of *d*-lactic acid on a medium containing glucose or starch, nutrient salts and calcium carbonate. Inulin was slowly converted into *d*-lactic acid.

ALCOHOLIC FERMENTATION PRODUCTS.

Ethyl Alcohol.—Alcohol is now recognised as a fairly common product of mould metabolism, particularly in certain genera. Thus all species of the genus *Fusarium* examined by Birkinshaw *et al.* (Phil. Trans. 1931, B, **220**, 93) produce alcohol in good yields. Anderson and Willaman (Proc. Soc. Exp. Biol. Med. 1922, **20**, 108) showed that *F. lini* affords alcohol in yields comparable with those obtainable from yeast fermentations, and the mechanism of its production is apparently similar in the two cases. Many species of *Mucor* give rise to an alcoholic fermentation and it was on this genus that the earliest observations of alcohol production were made.

The genera *Aspergillus* and *Penicillium* contain many species which produce alcohol, and it was found by Birkinshaw *et al.* (Phil. Trans. 1931, B, **220**, 27, 55), who examined and prepared balance sheets for 96 species of *Aspergillus* and 75 of *Penicillium*, that alcohol production is a characteristic of certain groups of morphologically related species, whilst it is not formed by other groups within the genus. Thus all members of the *A. flavus-oryzæ* group examined were found to give rise to some alcohol, but none could be detected in the *A. glaucus* group.

Acetaldehyde.—By interception by means of sulphite, acetaldehyde has been isolated by Cohen (Biochem. Z. 1920, **112**, 139) and Neuberg and Cohen (Biochem. Z. 1921, **122**, 204) from the metabolic products of various moulds when grown on glucose. Bernhauer and Thelen (*ibid.* 1932, **253**, 30) obtained up to 60% of the theoretical yield from sucrose by the agency of *A. niger*. Acetaldehyde can be isolated in small amounts from some moulds giving rise to alcoholic fermentation even in the absence of any interceptor.

Ethyl Acetate.—Ethyl acetate is a metabolic product of *Penicillium digitatum* Saccardo, when grown on glucose solution. It may arise by a modified Cannizzaro reaction from acetaldehyde (Birkinshaw *et al.* Phil. Trans. 1931, B, **220**, 355).

Glycerol.—This well known by-product of yeast fermentation is probably a fairly common metabolic product of moulds. It is formed by *Mucor racemosus* on sucrose (Emmerling, Ber. 1897, **30**, 454) and by species of *Aspergillus*, *Helminthosporium* and *Clasterosporium* (Birkinshaw *et al.* Phil. Trans. 1931, B, **220**, 153, 331). In view of the production of large yields of acetaldehyde by addition of sodium sulphite to the medium, it is probable that glycerol would be obtained in good yield by the same method, as is found in yeast fermentations (*v.* this Vol. p. 24).

REDUCTION PRODUCTS.

Glycerol, although dealt with above, is, like ethyl alcohol, a reduction product of sugar. Certain other polyhydric alcohols illustrating the reducing action of moulds remain to be considered.

Erythritol and Mannitol.—Erythritol was isolated by Oxford and Raistrick (Biochem. J. 1935, **29**, 1599) from the mycelium of *Penicillium brevi-compactum* Dierckx, together with mannitol, when the mould was examined before all the glucose had disappeared from the medium. Mannitol has frequently been recorded as a constituent of mycelium together with trehalose, but it can now be regarded as a true fermentation product since it can be obtained in large yield under suitable conditions. Thus Birkinshaw *et al.* (Phil. Trans. 1931, B, **220**, 153) were able to obtain yields up to 50% of the sugar utilised from the metabolism solution of a white species of *Aspergillus*. It was obtained in the largest yield when the air supply of the culture was restricted. It is also formed by species of other genera and is a main metabolic product of *Byssochlamys fulva* Olliver and Smith (Raistrick and Smith, Biochem. J. 1933, **27**, 1814). Coyne and Raistrick (*ibid.* 1931, **25**, 1513) found that the white *Aspergillus* giving high yields of mannitol was able to utilise for its production the hexoses, mannose, galactose and glucose and the pentoses, arabinose and xylose. Fructose, which yields mannitol by chemical reduction and is utilised by certain bacteria for the production of mannitol is not converted into mannitol by the mould.

All the products so far considered belong to the acyclic aliphatic series, and with the exception of citric acid, contain only straight carbon chains. Since they do not contain more than 6 carbon atoms they might conceivably be derived by direct degradation of the hexose. Many of the products now to be reviewed contain larger molecules which must obviously be obtained from sugar by synthetic processes.

HETEROCYCLIC COMPOUNDS (CARBON-OXYGEN RINGS).

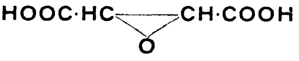
Oxidoethylene-$\alpha\beta$-dicarboxylic Acid.—This acid, $C_4H_4O_5$, is produced in yields of 10–20% of the sugar utilised when a species of *Monilia* is grown on a synthetic glucose medium, It is also formed from other sugars, polyhydric alcohols and related compounds. Citric and fumaric acids are also produced (Sakaguchi *et al.* Proc. Imp. Acad. Tokyo, 1937, **13**, 9; J. Agric. Chem. Soc. Japan, 1938, **14**, 362, 366; Zentr. Bakt. II, 1939, **100**, 302).

Kojic Acid.—Kojic acid, $C_6H_6O_4$, m.p. 152°, was isolated from the mycelium of *Aspergillus oryzæ* by Saito (Bot. Mag. Tokyo, 1907, **21**, 249).

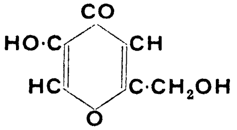
Yabuta determined its constitution as 5-hydroxy-2-hydroxymethyl-γ-pyrone. It has been obtained from several related species of *Aspergillus* belonging to the *flavus-oryzæ* group and also from *Penicillium Daleæ* Zaleski. The presence of kojic acid in the metabolism solution is readily recognised owing to the intense blood-red colour which it gives with ferric chloride. It can be obtained in large yield under suitable conditions, thus Katagiri and Kitahara claim yields of 63–66% from *Aspergillus oryzæ*, when grown on 5–20% glucose solutions at a p_H of 2·1.

2 - Hydroxymethylfurane - 5 - carboxylic Acid.—2-Hydroxymethylfurane-5-carboxylic acid, $C_6H_6O_4$, was obtained by Sumiki (Bull. Agric. Chem. Soc. Japan, 1929, **5**, 10; J. Agric. Chem. Soc. Japan, 1931, **7**, 819) from the metabolic products of *A. glaucus* grown on glucose or sucrose media. The acid is also formed by *A. clavatus, niger, oryzæ* and *wentii.*

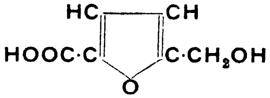
The pyrone and furane products may perhaps be derived from the pyranose and furanose sugars respectively if it is postulated that the mould is able first to synthesise the requisite hexose when the carbon is not supplied in this form. This condition is necessary since kojic acid is obtainable by fermentation not only of hexoses but also of mannitol, xylose, arabinose and glycerol.



Oxidoethylene-αβ-dicarboxylic acid.

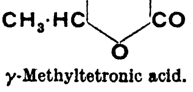


Kojic acid.

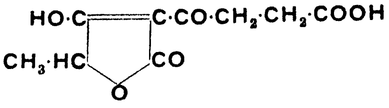


2-Hydroxymethylfurane-5-carboxylic acid.

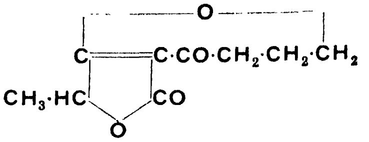
Tetronic Acid Series.—An interesting series of acids was obtained by Clutterbuck *et al.* (Biochem. J. 1934, **28**, 94; 1935, **29**, 300, 871, 1300) from *Penicillium charlesii*, a mould isolated from spoiled maize. These acids, *l-γ-methyltetronic acid*, $C_5H_6O_3$, m.p. 115°; *carolic acid*, $C_9H_{10}O_4$, m.p. 132°; *carolinic acid*, $C_9H_{10}O_6$, m.p. 129°; *carlic acid*, $C_{10}H_{10}O_6$, m.p. 176°, and *carlosic acid*, $C_{10}H_{12}O_6$, m.p. 181°, all contain the tetronic acid grouping and are related in structure to ascorbic acid. Later another member was added to the series, namely *terrestric acid*, $C_{11}H_{14}O_4$, m.p. 89°, obtainable by the agency of *P. terrestre* from glucose (Birkinshaw and Raistrick, Biochem. J. 1936, **30**, 2194). It is an ethyl carolic acid.



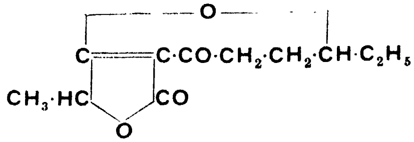
γ-Methyltetronic acid.



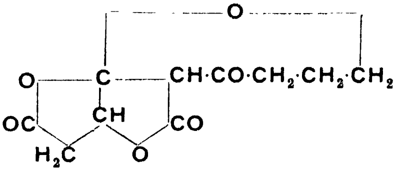
Carolinic acid.



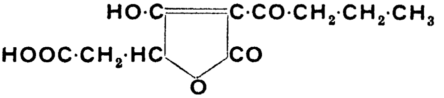
Carolic acid.



Terrestric acid.

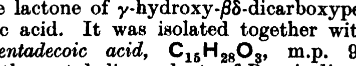


Carlic acid.



Carlosic acid.

Penicillic Acid.—Penicillic acid, $C_8H_{10}O_4$, m.p. 83–84°, in the lactone form has a molecular constitution not unlike that of the above series of acids. It was first isolated by Alsberg and Black (Bull. U.S. Bur. Pl. Ind. No. 270) from *Penicillium puberulum* Bainier, also an organism obtained from mouldy maize. It was obtained in fair yield from *P. cyclopium* by Birkinshaw *et al.* (Biochem. J. 1936, **30**, 394) and was shown to have the structure γ-keto-β-methoxy-δ-methylene-Δ^{α}-hexenoic acid or the corresponding hydroxylactone form.



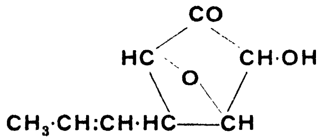
$$\underbrace{CH_2{:}CMe{\cdot}C(OH)C(OMe){:}CH{\cdot}CO}_{O}$$

Certain hydroxylated tribasic aliphatic acids which are found in the lactone form are also included in this group.

Spiculisporic Acid and Related Acids.—Spiculisporic acid, $C_{17}H_{28}O_6$, m.p. 145–146°, is the lactone of γ-hydroxy-βδ-dicarboxypentadecoic acid. It was isolated together with *γ-ketopentadecoic acid*, $C_{15}H_{28}O_3$, m.p. 92·6,° from the metabolic products of *P. spiculisporum* Lehman, by Clutterbuck *et al.* (Phil. Trans. 1931, B, **220**, 301). Birkinshaw and Raistrick (Biochem. J. 1934, **28**, 828) obtained a similar acid *minioluteic acid*, $C_{16}H_{26}O_7$, m.p. 171, from *P. minio-luteum* Dierckx, together with spiculisporic acid. Minioluteic acid has the constitution $\alpha\beta$-dihydroxy-$\beta\gamma$-dicarboxy-*n*-tetradecoic acid γ-lactone.

Carbocylic Compounds.

Terrein.—Terrein, $C_8H_{10}O_3$, m.p. 127°, is a neutral substance of highly reducing properties, isolated by Raistrick and Smith (Biochem. J. 1935, **29**, 606) from the metabolic products of *Aspergillus terreus* Thom, grown on a glucose medium. It was shown by Clutterbuck *et al.* (*ibid.* 1937, **31**, 987) to have the constitution 4-propenyl - 2 - hydroxy - 3:5 - oxido*cyclo*pentan - 1-one.



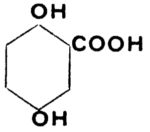
Palitantin.—Obtained by Birkinshaw and Raistrick (*ibid.* 1936, **30**, 801) from *Penicillium palitans*, palitantin, $C_{14}H_{22}O_4$, m.p. 163°, is an unsaturated hydroxyaldehyde, the constitution of which has not been completely determined. It probably contains a *cyclo*hexane ring.

Aromatic Series.

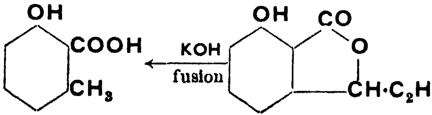
Benzene Derivatives.

Methylsalicylic Acid, Gentisic Acid and Mellein.—*Penicillium griseo-fulvum* Dierckx, according to the conditions under which it is grown, produces 6-hydroxy-2-methylbenzoic acid, $C_8H_8O_3$, m.p. 170–171°, giving an intense purple colour with $FeCl_3$, or gentisic acid (2:5-dihydroxybenzoic acid), giving a pure blue with ferric chloride (Anslow and Raistrick, *ibid.* 1931, **25**, 39; Raistrick and Simonart, *ibid.* 1933, **27**, 628).

Mellein, $C_{10}H_{10}O_3$, m.p. 58°, was obtained by Nishikawa (J. Agric. Chem. Soc. Japan, 1933, **9**, 772, 1059) from *Aspergillus melleus* Yukawa, and later by Yabuta and Sumiki (*ibid.* 1933, **9**, 1264; 1934, **10**, 703) from *A. ochraceus.* They showed that it is a lactone of 6-hydroxy-2-α-hydroxypropylbenzoic acid. On fusion with potash it is converted into 6-hydroxy-2-methylbenzoic acid.



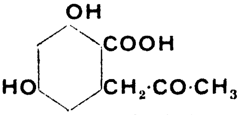
Gentisic acid.



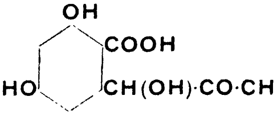
6-Hydroxy-2-methylbenzoic acid. Mellein.

Products of *Pencillium brevi-compactum.*—This organism has furnished a series of related compounds in the hands of Clutterbuck *et al.* (Biochem. J. 1932, **26**, 1441), Clutterbuck and Raistrick (*ibid.* 1933, **27**, 654) and Oxford and Raistrick (*ibid.* 1932, **26**, 1902; 1933, **27**, 634) which may all be regarded as derivatives of 2:4-dihydroxybenzoic acid.

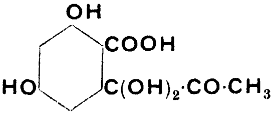
The most complex of these acids, *mycophenolic acid*, $C_{17}H_{20}O_6$, m.p. 141°, was probably first obtained in 1896 by Gosio, and later described by Alsberg and Black (Bull. U.S. Bur. Pl. Ind. No. 270) as a product of *P. stoloniferum* Thom. It yields a blue colour with ferric chloride. The constitution of this acid and the other acids from *P. brevi-compactum* are shown below:



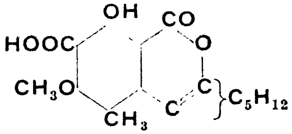
$C_{10}H_{10}O_5$.



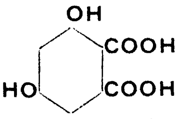
$C_{10}H_{10}O_6$.



$C_{10}H_{10}O_7$.



Mycophenolic acid, $C_{17}H_{20}O_6$.

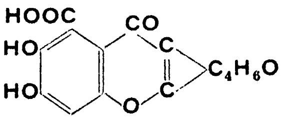


3:5-Dihydroxyphthalic acid, $C_8H_6O_6$.

Citromycetin.—Citromycetin,

$$C_{14}H_{10}O_7,2H_2O,$$

was obtained by Hetherington and Raistrick (Phil. Trans. Roy. Soc. 1931, B, **220**, 209) from various strains of *Citromyces* on a modified Czapek-Dox glucose medium. It crystallises in lemon-yellow needles darkening at 263°, m.p. 283–285° decomp., and affords an olive-green colour with ferric chloride. The constitution has not been completely determined but it may be represented as



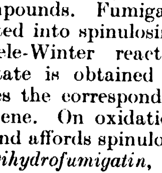
Fulvic Acid.—Fulvic acid is a yellow crystalline phenolic acid, $C_{14}H_{12}O_8$, m.p. 246°, isolated by Oxford *et al.* (Biochem. J. 1935, **29**, 1102) from the metabolic products of *Penicillium* *griseo-fulvum* Dierckx when grown on glucose solutions with ammonium salts as source of nitrogen. It gives a deep green colour with aqueous ferric chloride. It is obtained in larger yield from *P. flexuosum* Dale, and *P. brefeldianum* Dodge, and is found mostly in the mycelium of the latter organism.

QUINONES AND QUINONOID COMPOUNDS.

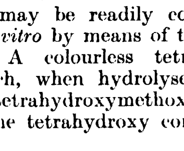
Benzoquinone Series.—Several compounds of this type have been isolated from the metabolic products of moulds. Birkinshaw and Raistrick (Phil. Trans. Roy. Soc., 1931, B, **220,** 245) obtained from strains of *Penicillium spinulosum* a methoxydihydroxytoluquinone, $C_8H_8O_5$, forming purple-black crystals, m.p. 201°. This was later given the name *spinulosin*, and shown by Anslow and Raistrick (Biochem. J. 1938, **32,** 687, 803) to have the constitution 3:6-dihydroxy-4-methoxy-2:5-toluquinone. A new product, *fumigatin*, $C_8H_8O_4$, obtained by these authors from *Aspergillus fumigatus*, crystallises in maroon-coloured needles, m.p. 116°. The constitution of fumigatin proved to be 3-hydroxy-4-methoxy-2:5-toluquinone. It thus differs from spinulosin in lacking one OH group present in that substance, the orientation of the other groups being the same in the two compounds. Fumigatin may be readily converted into spinulosin *in vitro* by means of the Thiele-Winter reaction. A colourless tetra-acetate is obtained which, when hydrolysed, gives the corresponding tetrahydroxymethoxytoluene. On oxidation the tetrahydroxy compound affords spinulosin.

Dihydrofumigatin, $C_8H_{10}O_4$, m.p. 99-101°, the quinol corresponding with fumigatin and obtainable from it by chemical reduction, was also isolated from the metabolism solution of *A. fumigatus*.

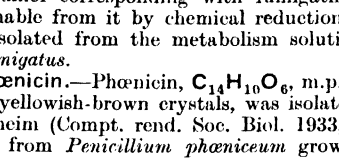
Phœnicin.—Phœnicin, $C_{14}H_{10}O_6$, m.p. 230-231°, yellowish-brown crystals, was isolated by Friedheim (Compt. rend. Soc. Biol. 1933, **112,** 1030) from *Penicillium phœniceum* grown on beer wort. On investigation by Posternak (Helv. Chim. Acta, 1938, **21,** 1326) it was found to have the constitution 4:4′-dimethyl-2:2′-dihydroxydiquinone. Phœnicin is thus closely related to fumigatin since it may be regarded as a product of union of 2 mol. of the latter with elimination of the methoxy groups.



Spinulosin.



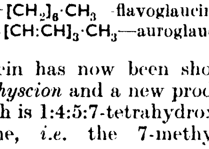
Fumigatin.



Phœnicin.

Friedheim has shown that phœnicin acts as a catalyst of biological oxidation, and it is surmised that all these quinones may form oxidoreduction systems and thus be of considerable importance in mould metabolism. It is significant in this connection that both fumigatin and its corresponding quinol have been isolated from the same metabolism solution. In the case of *Aspergillus glaucus*, two of the pigments isolated appear to have the quinol structure.

Aspergillus Glaucus Pigments.—Gould and Raistrick (Biochem. J. 1934, **28,** 1640) isolated from the mycelium of species of the *A. glaucus* series three crystalline pigments, *flavoglaucin*, $C_{19}H_{28}O_3$, m.p. 105°, *auroglaucin*, $C_{19}H_{22}O_3$, m.p. 152°, and rubroglaucin. More than 40% yields of crude pigments may be obtained from the dried mycelium. Auroglaucin is constituted similarly to flavoglaucin but contains three additional double bonds; the same substance, $C_{19}H_{30}O_3$, may be obtained from both pigments. They are probably derivatives of quinol and according to Cruickshank *et al.* (J.C.S. 1938, 2056) have the constitution:

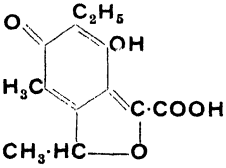


$R - [CH_2]_6 \cdot CH_3$ —flavoglaucin.
$R = [CH:CH]_3 \cdot CH_3$—auroglaucin.

Rubroglaucin has now been shown to be a mixture of *physcion* and a new product, *erythroglaucin*, which is 1:4:5:7-tetrahydroxy-2-methylanthraquinone, *i.e.* the 7-methyl ether of catenarin.

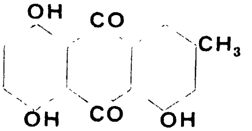
Chrysogenin.—Chrysogenin is a yellow pigment associated with a protein found in the metabolism solution of *P. chrysogenum* Thom, when grown on glucose medium (Clutterbuck *et al.* Biochem. J., 1932, **26,** 1907). It is microcrystalline, has a high rotation, $[\alpha]_{5461}$-762°, and gives an olive-brown colour with aqueous ferric chloride. It probably contains a quinol nucleus.

Citrinin.—Citrinin, $C_{13}H_{14}O_5$, m.p. 166-170° (decomp.), is a golden-yellow crystalline colouring matter obtained from *P. citrinum* Thom, on a modified Czapek-Dox glucose medium. It was isolated by Hetherington and Raistrick (Phil. Trans. Roy. Soc. 1931, B, **220,** 269). From a study of its breakdown products Coyne, Raistrick and Robinson (*ibid.* 1931, B, **220,** 297) assigned to it the quinonoid constitution:

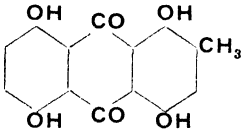


Anthraquinone Pigments.—The genus *Helminthosporium* has afforded an interesting range of pigments belonging to this group. *H. gramineum* Rabenhorst, when grown on a glucose medium, produces considerable amounts of crystalline hydroxyanthraquinones which are found in the mycelium and may compose up to 30% of its weight. The pigments consist of *helminthosporin*, $C_{15}H_{10}O_5$, and *catenarin*, $C_{15}H_{10}O_6$, in the ratio of 2–3:1 (Charles *et al.* Biochem. J. 1933, **27**, 499). *H. cynodontis* Marignoni, and *H. euchlaenae* Zimmermann, afford another hydroxyanthraquinone, *cynodontin*, $C_{15}H_{10}O_6$. A fourth member of this group, *tritisporin*, $C_{15}H_{10}O_7$, is produced by *H. tritici-vulgaris* Nisikado. All the species of *Helminthosporium* which have been found to yield hydroxyanthraquinone pigments in appreciable amount are comprised in the sub-genus *Cylindo-Helminthosporium*, whereas the members of the sub-genus *Eu-Helminthosporium* are lacking in these colouring matters.

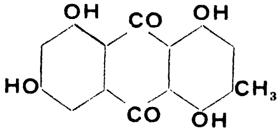
The constitutions assigned to these pigments are as follows (Raistrick *et al. ibid.* 1933, **27**, 1170; 1934, **28**, 559; 1940, **34**, 1124; J.C.S. 1933, 488):



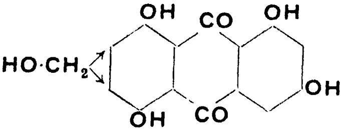
Helminthosporin.



Cynodontin.



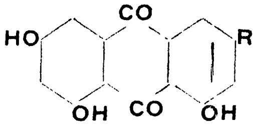
Catenarin.



Tritisporin.

In tritisporin the position of the $CH_2·OH$ group is uncertain but it must occupy one of the two positions indicated.

The formation of hydroxyanthraquinones is not to be regarded as a monopoly of the genus *Helminthosporium*. Various species of *Aspergilli* and *Penicillia* have recently been shown to produce these pigments. As already stated, erythroglaucin from *A. glaucus* is the 7-methyl ether of catenarin; it is associated in the mycelium with physcion or emodin monomethyl ether (4:5-dihydroxy-7-methoxy-2-methylanthraquinone) and its 9- and 10-anthranols (Ashley *et al.*, Biochem. J. 1939, **33**, 1291). Two derivatives of *frangula*-emodin (4:5:7-trihydroxy-2-methylanthraquinone) were obtained by Anslow *et al.* (*ibid.* 1940, **34**, 159) as metabolic products of a strain of *P. cyclopium* Westling. These were identified as ω-hydroxyemodin ($R=CH_2·OH$) and emodic acid ($R=COOH$).



The pigment obtained by Posternak (Compt. rend. soc. phys. hist. nat. Genève, 1939, **56**, 28) from *P. citreo-roseum* was found by direct comparison to be ω-hydroxyemodin.

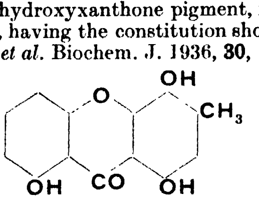
From *P. carmino-violaceum* Biourge grown on a glycerol–salts medium Hind (Biochem. J. 1940, **34**, 67) obtained two new hydroxyanthraquinones, *carviolin*, $C_{16}H_{12}O_6$, and *carviolacin*, $C_{20}H_{16}O_7$, which are derivatives of 2-methylanthraquinone. Carviolin, chrome-yellow crystals, m.p. 286°, has been shown (*ibid.* 1940, **34**, 577) to be a monomethyl ether of ω-hydroxyemodin. Carviolacin, light brown needles, m.p. 243° (decomp.) is also a monomethyl ether and yields 2-methylanthracene on zinc dust distillation.

Igarasi (J. Agric. Chem. Soc. Japan, 1939, **15**, 225) believes the colouring matter *funiculosin*, $C_{15}H_{10}O_5$, obtained from *P. funiculosum* cultures, to be a trihydroxymethyl- or a (hydroxymethyl)-dihydroxy-anthraquinone although he obtains anthracene not methylanthracene on zinc dust distillation.

Penicilliopsin.—This colouring matter, obtained from culture of *Penicilliopsis clavariaeformis* grown in the dark was characterised by Oxford and Raistrick (Biochem. J. 1940, **34**, 790). Penicilliopsin, $C_{30}H_{24}O_8$, orange prisms, m.p. 330° (decomp.), is oxidised in air in suitable solvents to *oxypenicilliopsin*, $C_{30}H_{20}O_9$, purple-black crystalline aggregates, m.p. above 360°, solutions of which on exposure to light are converted into an isomeric irradiation product consisting of chocolate-brown needles of m.p. above 370°, which give intensely fluorescent solutions. The colouring matter from naturally occurring specimens of *P. clavariaeformis*, which was formerly known as mycoporphyrin, was no doubt a mixture of penicilliopsin and its conversion products. Irradiated oxypenicilliopsin is closely related to, but not identical with, hypericin, the colouring matter of St. John's wort, *Hypericum perforatum*, which causes a condition of light sensitiveness in animals.

Since penicilliopsin gives *frangula*-emodin-anthranol on heating alone and tetranitroemodin on oxidation with nitric acid it may be a polyhydroxy derivative of a reduced *meso*dimethyldianthrone.

Ravenelin.—The mycelia of *Helminthosporium ravenelii* Curtis, and *H. turcicum* Passerini, grown on a glucose medium, contain a crystalline trihydroxyxanthone pigment, ravenelin, $C_{14}H_{10}O_5$, having the constitution shown below (Raistrick *et al.* Biochem. J. 1936, **30**, 1303):

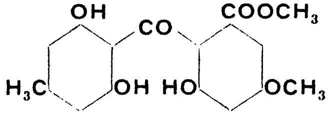


Ravenelin.

OTHER CRYSTALLINE METABOLIC PRODUCTS OF UNKNOWN CONSTITUTION.

Product.	Empirical formula.	M.P.	Appearance, etc.	$FeCl_3$ colour.	Organism.	Isolated by
Puberulic acid	$C_8H_6O_6$	316° (decomp.)	Cream coloured	Reddish-brown	*P. puberulum* Bainier	Birkinshaw and Raistrick, Biochem. J. 1932, **26**, 441.
Related acid	$C_8H_4O_6$	296° (decomp.)	Yellow plates	Reddish-brown	*P. aurantio-virens* Biourge	
Glauconic acid	$C_{18}H_{20}O_7$	202°	Colourless prisms	None	"*P. glaucum*"	Wijkman, Annalen, 1931, **485**, 61. *Cf.* Sutter and Wijkman, Annalen, 1935, **519**, 97; 1936, **521**, 189.
Glaucanic acid	$C_{18}H_{20}O_6$	186°	" "		"	
Pigment	$C_{19}H_{22}O_4$	124°	Orange-coloured prisms		"	
"	?		Red (contains N)		"	
Byssochlamic acid	$C_{18}H_{20}O_7$	163·5°	Colourless prisms		*Byssochlamys fulva* Olliver and Smith	Raistrick and Smith, Biochem. J. 1933, **27**, 1814.
Glaucic acid	$C_{17}H_{22}O_5$	237–238°			*A. glaucus*	Sumiki, J. Agric. Chem. Soc. Japan, 1933, **9**, 714.
Monascorubrin	$C_{22}H_{24}O_5$	136°	Red prisms		*Monascus purpureus* Went	Nishikawa, Bull. Agric. Chem. Soc. Japan, 1932, **8**, Nos. 4–6.
Monascoflavin	$C_{17}H_{22}O_4$	145°	Yellow plates		" " "	
Oosporin	$C_{10}H_{14}O_2$	176° (decomp.)	Colourless prisms	Purple-brown	*Oospora aurantia* (Cooke) Sacc. and Vogl	Nishikawa, Proc. Imp. Acad. Japan, 1934, **10**, 414.
Aurantin	$C_{16}H_{22}O_3$	183° (decomp.)	Yellow needles	" "		
Product A	$C_{17}H_{16}O_8$ (or $C_{19}H_{18}O_9$)	214°	Needles	Violet (in EtOH)	*Oospora sulphurea-ochracea*	Nishikawa, Bull. Agric. Chem. Soc. Japan, 1936, **12**, 47; 1937, **13**, 1.
" B	see Sulochrin (p. 57)					
" C	$C_{17}H_{16}O_8$	200° (decomp.)	Rhombs	None	" " "	
" D	$C_{18}H_{18}O_8$ (?)	190°		Violet (in EtOH)	" " "	
" E	$C_{17}H_{14}O_7$	147°	Pale yellow	None	" " "	
" F	$C_{16}H_{14}O_8$	239° (decomp.)			" " "	
" G	?	205°	Pale yellow prisms		" " "	
Rubrofusarin	$C_{15}H_{12}O_5$	210–211°	Glistening red plates	Greenish-brown (in EtOH)	*Fusarium culmorum* (W. G. Smith) Sacc.	Ashley *et al.* Biochem. J. 1937, **31**, 385.
Aurofusarin	$C_{30}H_{20}O_{12},H_2O$	above 360°	Orange-yellow prisms		" " "	
Culmorin	$C_{15}H_{26}O_2$	175°	Thick colourless needles	None	" " "	
Luteoleersin	$C_{26}H_{38}O_7$	135°	Yellow rods	None	*Helminthosporium leersii* Atkinson	Ashley and Raistrick, Biochem. J. 1938, **32**, 449.
Alboleersin	$C_{26}H_{40}O_7$	215–216°	Colourless silky needles	Yellow	" " "	

Sulochrin.—Nishikawa (Acta Phytochim. 1939, **11**, 167) extracted from the mycelium of *Oöspora sulphurea-ochracea* van Beyma a number of crystalline products labelled A to G which are, with one exception, of unknown constitution. The exception is product B, $C_{17}H_{16}O_7$, yellow needles, m.p. 262°, which has been named sulochrin and to which the following constitution has been given:



It is evidently closely related to the chlorine-containing compounds geodin and erdin (*see* p. 58).

STEROLS.

A number of references are found in the literature to the isolation of sterols from the mycelium of the lower fungi, but owing to the difficulties of separation many of the products obtained were probably mixtures.

Ergosterol.—Ergosterol has, however, been separated and characterised by methods which put its identity beyond doubt. The yields obtained are variable, depending on the organism and the method of cultivation. Heiduschka and Lindner (Z. physiol. Chem. 1929, **181**, 15) determined the ergosterol content of *Dematium pullulans*, *Penicillium glaucum* and *Aspergillus oryzæ* as 0·30, 0·75 and 0·46% respectively of the dry matter. Sumi (Biochem. Z. 1928, **195**, 161; 1929, **204**, 412) isolated 0·08% of crude ergosterol from the spores of *A. oryzæ*, and Takata (J. Soc. Chem. Ind. Japan, 1929, **32**, 157 [B]; Suppl. 268) obtained a yield of 0·028% from the mycelium of the dried organism.

The sterol formed by *P. puberulum* Bainier, when grown on a Czapek-Dox medium containing glucose as sole source of carbon, was isolated and characterised by Birkinshaw *et al.* (Biochem. J. 1931, **25**, 1977). Final proof of its identity with ergosterol was afforded by its absorption spectrum and its antirachitic activity acquired after irradiation. This affords direct evidence of the synthesis of ergosterol from glucose.

Ergosterol is found in mould mycelium not only in the free state but also as esters. Oxford and Raistrick (*ibid.* 1933, **27**, 1176) isolated crystalline ergosteryl palmitate from the mycelium of 14 out of 15 strains of *P. brevi-compactum* Dierckx, and from the mycelium of *P. italicum* Wehmer. *P. aurantio-griseum* Dierckx var. *poznaniensis* Zaleski, was found to contain as much as 0·5% of the ester.

FATS AND LIPINS.

Fats and oils are of general occurrence in mould mycelium and can be obtained by extraction of the dried material with light petroleum or ether. The quantity of fat can be greatly increased by adopting special conditions of culture, and seems to be favoured by a high sugar content of the medium. Thus Ward *et al.* (Ind. Eng. Chem. 1935, **27**, 318), following on earlier work of Lockwood *et al.* (Z. Bakt. II, 1934, **90**, 411) found that when *P. javanicum* was grown on a medium containing 40% of glucose the mycelium contained up to 41·5% of fat.

The composition of the fat has been quantitatively examined in some cases. Ward and Jamieson (J. Amer. Chem. Soc. 1934, **56**, 973) report that the saturated acids obtained by hydrolysis of the oil amounted to 30·8% of the total weight. They consisted of palmitic 69·5%, stearic 28% and *n*-tetracosoic acid 2·5%. The unsaturated acids (60·8% of the total oil) consisted of oleic 52·1%, and α- and β-linoleic acid 47·9%.

The lipins of *A. sydowi* were examined by Strong and Peterson (*ibid.* 1934, **56**, 952). They obtained 22% of free fatty acids and a phospholipin which was separated as a complex with magnesium chloride. The fatty acids (free and combined) consisted of palmitic 8·8%, stearic 11%, *n*-tetracosoic 0·9%, oleic 29·6%, linoleic 16·3% and higher unsaturated acids 1·7%. The water-soluble fraction obtained after saponification of the fats consisted largely of glycerol. Woolley *et al.* (*ibid.* 1935, **57**, 2589) have examined the phospholipin fraction of *A. sydowi*. The phospholipins (0·4–0·7 by weight of the mycelium) consist of a mixture of lecithin and kephalin. On acid hydrolysis they yield glycerophosphoric acid, choline, cholamine and oleic acid as chief products.

The fat from *A. niger* mycelium obtained from a technical citric acid fermentation on molasses medium had the following composition (Bernhauer and Posselt, Biochem. Z. 1937, **294**, 215); glycerol 6·2%, total fatty acids 67·5%, saturated fatty acids 13·0% (palmitic 7·1, stearic 0·9, lignoceric 1·8), unsaturated fatty acids 45·4% (oleic 21·5, α-linoleic 23·9) unsaponifiable 12·0% (ergosterol 1·4, other constituents 10·6).

POLYSACCHARIDES.

A number of complex polysaccharides derived from moulds have been recorded and the products of hydrolysis examined. These cover most of the simpler natural sugars and it is noteworthy that the monosaccharides which are employed in building up the complex molecule appear to bear no relation to the sugar used as substrate for the mould.

"Spore starch" or "mould starch," which gives a blue colour with iodine, has been obtained from various species of *Aspergillus* and *Penicillium*. Whether the products from these different organisms are identical seems open to doubt. Schmidt (Biochem. Z. 1925, **158**, 223) concluded that mould starch is identical with amylose and therefore with *iso*lichenin. The production of the material by *A. niger* is favoured by a strongly acid medium and its accumulation may be due to inhibition of the diastase present in the mould by the acid (Hida, J. Shanghai Sci. Inst. 1934, [iv], **1**, 85).

From the mycelium of *P. puberulum*, Alsberg and Black (Bull. U.S. Bur. Pl. Ind. No. 270) obtained a substance giving a violet colour with iodine and supposed by them to be identical with trehalum from manna. Dox and Neidig (J. Biol. Chem. 1914, **18**, 167; **19**, 235) isolated from *P. expansum* mycodextran and from

A. niger mycogalactan, giving respectively glucose and galactose on hydrolysis. Neither polysaccharide gave a colour with iodine. Birkinshaw *et al.* (Phil. Trans. Roy. Soc. 1931, B, **220**, 153, 331, 355) obtained from a white *Aspergillus* a polysaccharide resembling glycogen. *Fumago vagans* and *Penicillium digitatum* gave polysaccharides affording glucose on hydrolysis and giving no colour with iodine.

In certain cases the constitution of the polysaccharide molecule has been determined. *P. charlesii* G. Smith, when grown on a glucose medium, yields two polysaccharides: *mannocarolose*, consisting only of mannose residues, and *galactocarolose*, consisting only of galactose residues (Clutterbuck *et al.* Biochem. J. 1934, **28**, 94). Mannocarolose has a chain length of 8–9 units of *d*-mannopyranose linked through the 1:6-positions, a unique structure for a polymannose (Haworth *et al.* Biochem. J. 1935, **29**, 612). Galactocarolose is composed of a chain of about nine *β*-galactofuranose units linked through the 1:5 positions (Haworth *et al. ibid.* 1937, **31**, 640). *Varianose*, a polysaccharide obtained from *P. varians* G. Smith, is constituted of a chain of 6–8 *β*-galactopyranose units with a glucopyranose unit as one end of the chain and a unit of either *d*-idose or *l*-altrose at the reducing end (Haworth *et al. ibid.* 1935, **29**, 2668).

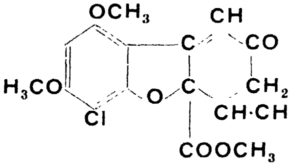
Luteic acid was obtained by Raistrick and Rintoul (Phil. Trans. Roy. Soc. 1931, B, **220**, 255) as a metabolic product of a non-ascosporic form of *P. luteum* Zukal, grown on a Czapek-Dox glucose medium. The acid has a high molecular weight and on acid hydrolysis affords glucose and malonic acid. With dilute barium hydroxide the malonic acid is removed and a neutral polysaccharide *luteose* is obtained giving only glucose on hydrolysis. Luteic acid is obtainable not only from glucose but also from fructose, mannose, galactose, xylose, arabinose and glycerol (Birkinshaw and Raistrick, Biochem. J. 1933, **27**, 370). A polymannose and a polygalactose are also synthesised by the mould in smaller amounts, the former being produced in the early stages and the latter in the later stages of growth (Anderson and Raistrick, *ibid.* 1936, **30**, 16).

COMPOUNDS CONTAINING ELEMENTS OTHER THAN CARBON, HYDROGEN AND OXYGEN.

Arsenic Compounds.—Various cases of arsenical poisoning have been found to be caused by the action of mould growth on damp wall-papers containing arsenic. (*v.* ARSENICALS, ORGANIC, Vol. I, p. 483.)

Chlorine Compounds.—A strain of *A. terreus* Thom, when grown on Czapek-Dox solution containing KCl as the sole source of chlorine, gives rise to two yellow crystalline metabolic products, *geodin*, $C_{17}H_{12}O_7Cl_2$, m.p. 235° (decomp.), $[\alpha]_{5461}+179°$ in chloroform and *erdin*, $C_{16}H_{10}O_7Cl_2$, m.p. 211° (decomp.), optically inactive (Raistrick and Smith, *ibid.* 1936, **30**, 1315). These two compounds are closely related in structure, geodin being the dextro-rotatory isomeride of a monomethyl ether of the optically inactive erdin (Clutterbuck *et al. ibid.* 1937, **31**, 1089). The constitution of dihydrogeodin trimethyl ether has been shown to be *methyl 3′:5′-dichloro-4:6:2′:6′-tetramethoxy-4′-methylbenzophenone-2-carboxylate* and of dihydroerdin trimethyl ether to be *3′:5′-dichloro-4:6:2′:6′-tetramethoxy-4′-methylbenzophenone-2-carboxylic acid* (Calam *et al., ibid.* 1939, **33**, 579).

Another chlorine-containing compound, namely *griseofulvin*, $C_{17}H_{17}O_6Cl$, m.p. 218–219°, was isolated by Oxford *et al., ibid.* 1939, **33**, 240) from the mycelium of *Penicillium griseofulvum* Dierckx, grown on a modified Czapek-Dox medium. A provisional structural formula was advanced:



In view of these discoveries a quantitative survey was made by Clutterbuck *et al.* (*ibid.* 1940, **34**, 664) of the chlorine metabolism of 139 species or strains of moulds grown on Czapek-Dox 5% glucose medium containing 0·05% of KCl as sole source of chlorine. Of the species or strains examined 57 utilised less than 5% of the KCl; 77 utilised 5–25% of the KCl (this group includes *P. griseofulvum*); only 5 cultures metabolised more than 25% of KCl. Two of these were strains of *A. terreus* Thom, one of which produces geodin and erdin, another was *Absidia spinosa* Lindner, and the remaining two were strains of *Caldariomyces fumago* Woronichin. From the last-named fungus a new product, *caldariomycin*, was obtained by ether extraction of the metabolism solution. Caldariomycin, $C_5H_8O_2Cl_2$, m.p. 121°, probably has the constitution 2:2-dichloro*cyclo*pentane-1:3-diol, and is thus akin to terrein which also contains the *cyclo*pentanone ring.

It is noteworthy that *C. fumago* also converts KBr, when present in the same medium in place of KCl, into organic bromine-containing metabolic products which have not yet been isolated in a state of purity.

Nitrogen Compounds.—Oxford *et al.* (*ibid.* 1935, **29**, 1102) obtained from the mycelium of *P. griseo-fulvum* Dierckx, a colourless crystalline nitrogenous substance, $C_{22}H_{28}O_5N_2$ which is an acid and yields a hydrocarbon on hydrolysis. Another crystalline nitrogenous product, $C_{40}H_{79}O_5N$, was isolated from the mycelium of *P. brefeldianum* Dodge. Woolley and Peterson (J. Biol. Chem. 1938, **122**, 213) recorded the isolation from the dried mycelium of *A. sydowi* of cyclic choline sulphate in 0·26% yield. This was obtained both from autolysate and from an acetone extract of the defatted mycelium.

Proteins are elaborated by the lower fungi as necessary constituents of the cell, but they are sometimes excreted into the metabolism solution. The protein found in the metabolism solution of *P. chrysogenum*, in association with the pigment, closely resembles a typical alkali-soluble leaf protein (Clutterbuck *et al.* Biochem.

J. 1932, **26**, 1907). Gorcica *et al.* (*ibid.* 1934, **28**, 504), by fractionation of the nitrogenous products of the mycelium of *A. fischeri*, obtained 30% of water-soluble non-protein nitrogen, 55% of alkali-soluble protein nitrogen and 12% of alkali-insoluble residual nitrogen. The alkali-soluble protein contained one fraction precipitated by acids and a second acid-soluble fraction precipitated by copper sulphate solution. The residue contained 2·3% of nitrogen, of which 62% was glucosamine nitrogen. Glucosamine was also identified in the hydrolysis products of *P. javanicum* by May and Ward (J. Amer. Chem. Soc. 1934, **56**, 1597).

The constituent amino acids of the mould proteins have not been fully investigated, although feeding experiments on rats have shown that the proteins of *A. sydowi* are insufficient for maintaining growth unless supplemented by proteins from other sources (Gorcica *et al.* J. Nutrition, 1935, **9**, 701).

ENZYMES.

Moulds contain a rich variety of enzymes, some of which have industrial applications.

Gallic Acid Fermentation—Gallic acid is prepared from the glucoside tannin by the action of the hydrolytic enzyme *tannase* which is produced by the growth of *A. niger* on solutions containing tannin and suitable nutrients. The enzyme can then be separated and used to hydrolyse solutions of pure tannin to gallic acid.

In the old industrial process ground gall-nuts, which contain a high percentage of tannin, were moistened, piled in heaps, and maintained at about 30°. The heaps were stirred at intervals. Moulds developed throughout the mass and after about a month the gallic acid was leached out. The process has been much improved and clear tannin extract is now used. The sterile extract is inoculated with a species of *Aspergillus*, and the solution is agitated by blowing air through it. When the tannin has entirely disappeared the gallic acid is recovered from the liquor.

Oriental Food Fermentations.—The saké fermentation, shoyu making and numerous other fermentations practised in the Orient make use of species of *Aspergilli* as well as mucors, yeasts and bacteria in their empirical production of foods and liquors. These fermentations usually make use of a starter (koji) which consists of masses of rice, soya beans, or other material from previous successful fermentations for use in the production of successive fermenting mashes, or for commercial distribution.

The *saké fermentation* utilises the diastatic activity of *A. oryzæ* for the saccharification of the starch of rice for fermentation purposes. The alcohol production is said to be due to the yeasts present. Certain selected strains of the organism with high diastatic power are propagated and sold under the name of "*Tane-koji*" or "*Saké-koji.*"

In the *soy fermentation* the proteolytic activity of the moulds (*flavus-oryzæ* group) is the important factor. The soya bean contains a high percentage of protein which is hydrolysed by the agency of the strains selected for their protease activity although carbohydrate fission is not entirely suppressed. For soy sauce the koji is immersed in a brine of high sodium chloride content, and the digestion proceeds slowly. Yeasts are also believed to play some part in the process. The finished product is a dark salty liquid which is used as a component of table sauces in Europe and America.

"*Tamari*" is another sauce which owes its individual flavour to the use of a specific mould, *A. tamarii.*

"*Miso*" is prepared by mixing cooked soya beans with an *Aspergillus* koji, adding salt and ripening the mixture.

Fish Fermentation.—A series of fermented products are prepared by the Japanese from fish; in some of these moulds are the active agents in producing the flavour and qualities desired. The product *Katsuobushi* is obtained by cutting the fish (of the tuna group) into strips, cooking, packing in masses and fermenting. The material is then dried for commercial distribution. *Aspergilli* belonging to the *flavus-oryzæ* group, the *ochraceus* group and the *glaucus* group have at different times been claimed as the active agents of this fermentation.

Taka-diastase.—Takamine and his associates have studied the enzymic activities of the *A. flavus-oryzæ* group and have patented the preparation of a number of products such as taka-diastase, and enzymic mixtures such as "polyzime." The production of these materials is based on the use of a cheap, bulky, fibrous, nutrient base which is sterilised, moistened, inoculated with spores of the selected organism and incubated at the desired temperature. Growth is interrupted at the time of maximum enzymic activity and the commercial product is obtained by drying the mass or by extraction of the enzymes and subsequent purification. The product is naturally a mixture of enzymes, not a single active principle. Such crude enzyme mixtures are used in the desizing of textiles.

Cheese Ripening.—The enzymes of moulds play a large part in the ripening of certain varieties of cheese. The Camembert-Brie group of cheeses obtain their texture from the proteolytic activity of *P. camemberti* Thom. In the ripening process which is conducted at 50–60° F. the surface of the cheese becomes covered with a floccose white mantle of mould. In about 10 days the mould becomes bluish- or greenish-gray from developing conidia and the curd in contact with the mycelium begins to soften to a smooth buttery texture. The reaction changes from acid to alkaline to litmus as the softening progresses inward. In about 4 weeks the entire mass is softened. The change is associated with a proteolytic enzyme similar to erepsin which produces abundant caseoses but no putrefactive products. *P. caseicolum* produces a cheese of somewhat different texture. According to Mazé, however, the peptonisation is not due to the enzymes of moulds, whose function is rather to destroy the lactic acid present and thus make the reaction of the medium favourable for the *casease* of the lactic enzymes everywhere present.

In the group of green cheeses such as Roquefort, Gorgonzola and Stilton the active organism is *P. roqueforti.* The cheese is here more open in texture and the mould develops throughout the mass giving it the characteristic green marbled appearance. The Roquefort mould can withstand a lower oxygen tension than any other species examined by Thom and Currie (J. Biol. Chem. 1913, **15**, 249) and hence is able to dominate the flora of the crevices within the cheese. Currie showed that the characteristic flavour of this group of cheeses is due to the splitting of the butter fat by the mould to produce a mixture of fatty acids different from that produced by bacterial activity.

J. H. B.

FERNANDINITE. A hydrated calcium vanadyl vanadate, $CaO{\cdot}V_2O_4{\cdot}5V_2O_5{\cdot}14H_2O$, forming compact masses of a dull-green colour or minutely crystallised as rectangular plates. It dissolves readily in acids to a green solution, and sufficiently in cold water to give a yellow solution. It occurs as an alteration product of *patronite* at Minasragra in Peru.

L. J. S.

FERONIA GUM. Wood-apple gum obtained from *Feronia elephantum* Correa (Fam. Rutaceæ).

FERRITE. This term has unfortunately several different meanings. To the chemist it implies a salt in which ferric oxide plays the part of an acid, for example, barium ferrite $BaFe_2O_4$. In a mineralogical sense it was first applied by H. Vogelsang, in 1872, to an amorphous iron hydroxide, of unknown composition, which, as red and yellow particles, is present in many partly decomposed igneous rocks. In this sense the term has been used by certain petrologists for the patches of indefinite ferruginous alteration products seen under the microscope in thin sections of rocks. The same name has also been applied to ferruginous pseudomorphs after olivine occurring in the doleritic rocks of the neighbourhood of Glasgow (M. F. Heddle, Min. Mag. 1882, 1887). It has also been much used by metallographers, following H. M. Howe (The Metallurgy of Steel, 1890), for pure metallic iron, which, together with iron carbide, etc., forms one of the microscopic constituents of iron and steel. Later, the same name was applied by V. I. Vernadsky, in his Russian "Treatise on Mineralogy," (St. Petersburg, 1908), to native iron, for example, the terrestrial iron from Ovifak on Disko Island, Greenland.

L. J. S.

FERRITUNGSTITE. Mineral form of hydrated ferric tungstate, $Fe_2O_3{\cdot}WO_3{\cdot}6H_2O$ (Schaller, Amer. J. Sci. 1911, [iv], **32**, 161).

FERROAXINITE (Vol. I, 560*d*).

FERROBRUCITE (Vol. II, 119*b*).

"FERROCHLORE" (Vol. IV, 21*d*).

FERROCHROME (Vol. III, 105*d*).

FERROTUNGSTEN. An alloy of iron with tungsten usually containing 80–85% of the latter.

FERRUCCITE. Sodium fluoborate,

$$NaBF_4,$$

occurring as minute orthorhombic crystals, together with *avogadrite* KBF_4, *malladrite* Na_2SiF_6, *hieratite* K_2SiF_6, and *sassolite* H_3BO_3, in saline encrustations from fumaroles in the crater of Vesuvius. Named after Ferruccio Zambonini (1880–1932) of Naples (G. Carobbi, Periodico Min. 1933, **4**, 410).

L. J. S.

FERSMANITE. Titano-silicate and fluoride of calcium and sodium,

$$2Na_2(O,F_2){\cdot}4CaO{\cdot}4TiO_2{\cdot}3SiO_2,$$

occurring as monoclinic crystals, previously mistaken for sphene, in nepheline-syenite from the Kola peninsula, northern Russia (A. N. Labuntzov, Compt.rend. Acad. Sci. U.R.S.S. 1929, 297).

L. J. S.

FERULIC ACID, $C_{10}H_{10}O_4$. *m*-Methoxy-*p*-hydroxy-cinnamic acid,

$$MeO{\cdot}C_6H_3(OH)CH{:}CH{\cdot}CO_2H,$$

occurs in asafœtida resin (Hlasiwetz and Barth, Annalen, 1866, **138**, 64); in opopanax (Tschirch and Knitl, Arch. Pharm. 1899, **237**, 256); in the resin of the black fir (Bamberger, Monatsh. 1891, **12**, 441); and in various other resins (Karrer and Schwarz, Chem. Zentr. 1932, II, 1639). The alcoholic extract of asafœtida resin is precipitated with lead acetate, and the precipitate of lead ferulate is decomposed with sulphuric acid. It can be synthesised by several methods: by means of Perkin's reaction by heating together vanillin, acetic anhydride and dry sodium acetate, and decomposing the acetylferulic acid thus formed with potash (Tiemann and Nagai, Ber. 1878, 11, 647); by treating the methyl ether of *p*-amino-*m*-coumaric acid with sodium nitrite and decomposing the diazo-compound thus produced with water (Ulrich, Jahresber. 1885, 2093; *cf.* G.P. 32914; Frdl. 1. 588); and by warming a mixture of vanillin and malonic acid in pyridine solution with a little piperidine (Robinson and Shinoda, J.C.S. 1925, **127**, 1973; Dutt, J. Indian Chem. Soc. 1925, **1**, 297). Rhombic needles, m.p. 168–169°, almost insoluble in cold water, readily soluble in alcohol, less soluble in ether (Tiemann and Nagai, Ber. 1876, **9**, 416). The solution gives with lead acetate a yellow flocculent precipitate, with ferric chloride a yellowish-brown precipitate, and reduces silver nitrate and Fehlings' solution on warming. Fusion with caustic potash converts it into acetic and protocatechuic acids. It is easily decarboxylated by copper powder in quinoline to give a good yield of the corresponding styrene, which has a strong odour of cloves (Fromm, Annalen, 1927, **456**, 168; Reichstein, Helv. Chim. Acta, 1932, **15**, 1450). It is reduced by sodium amalgam or $Pd/CaCO_3$ in hydrogen to the dihydro-acid, $C_{10}H_{12}O_4$, m.p. 89–90° (Brand and Westerburg, Arch. Pharm. 1931, **269**, 326). With methyl-alcoholic sulphuric acid it gives a dimeric methyl ester, which can be hydrolysed to the dimeric acid, but ethyl and propyl alcohols give the normal esters (Tanaka, Sci. Rep. Tôhoku Imp. Univ. 1929, **18**, 619). With methyl sulphate it yields 3:4-dimethoxy-cinnamic acid (Robinson and Shinoda, J.C.S. 1925, **127**, 1973). Oxidation of the acid with ferric chloride in aqueous-alcoholic solution leads to dehydrodiferulic acid, $C_{20}H_{18}O_8$, m.p. 202–205° (sinters at 195°) (Erdtman, Svensk Kem. Tidskr. 1935, **47**, 223). Certain substituted amides of ferulic acid form compounds with acids and ammonia, *e.g.* the benzylamide, $C_{17}H_{17}O_3N$, gives compounds with $\frac{1}{2}H_2SO_4$, H_2SO_4, HCl and NH_3 (Kobayashi, Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **6**, 185). For a microchemical test for ferulic acid in pharmaceutical products, *see* Rosenthaler, Pharm. Zentr. 1926, **67**, 353.

iso*Ferulic Acid* is *m*-hydroxy-*p*-methoxycinnamic acid; it is also known as *Hesperitinic acid* (Tiemann and Will, Ber. 1881, **14**, 948).

FERVANITE. Hydrated vanadate of iron, $2Fe_2O_3{\cdot}2V_2O_5{\cdot}5H_2O$. A golden-brown fibrous (monoclinic) mineral, suggestive of stained gypsum, occurring with vanadium and uranium impregnations in sandstone in Grant Co., Utah, and San Miguel Co., Colorado (E. P. Henderson and F. L. Hess, Amer. Min. 1931, **16**, 273).

L. J. S.

FERTILISERS or MANURES. Either of these terms might properly be applied to any material added to the soil for the purpose of increasing its fertility, and, in this sense, would be extended to include lime, chalk, marl and even clay and sand. In common practice, however, the term " manure " or " fertiliser " is restricted to materials the main function of which is to convey directly to the soil some constituent or constituents of plant food, to the exclusion of those of which the fertilising action is mainly indirect, consisting in the improvement of the physical condition of the soil or the development of its inherent or natural chemical resources. It has been long recognised that the chief constituents of plant food which are naturally taken up from the soil are nitrogen, phosphorus, sulphur, potassium, calcium, magnesium and iron, together with the perhaps less important constituents silicon, chlorine and sodium. Modern work, however, has shown that minute quantities of other elements—notably boron and manganese—are essential factors in the healthy growth of many plants, and it appears possible that minute traces of copper, zinc, cobalt and perhaps other elements of long unsuspected importance may also play a part in plant nutrition (*v.* Ash).

Apart from calcium—the artificial supply of which is necessary in special cases only—nitrogen, phosphorus and potassium are, however, the most important constituents to be applied as manure, as they are those in which the soil is most generally deficient.

Manures or fertilisers are sometimes classified as " natural " and " artificial," but the dividing line is not easily drawn. In the present article we shall briefly consider the principal substances employed as manures or fertilisers, passing on to observations as to the relative utility of some of them, and shall then refer to the special methods employed for their analysis.

Farmyard Manure.—Farmyard manure and stable manure are composed of litter mixed with the excreta of animals. The litter in farmyards is usually straw, but this has been to a large and increasing extent superseded in stables by dried and shredded peat moss. In some parts of the country bracken is used for litter, and in hop districts hop-bine is thus worked up into manure. The composition of the manure depends initially to some extent on the nature of the litter, but to a greater extent on the length of time the litter has been in use, the number and kind of animals littered on it, and the quantity and quality of the food consumed by them. Its final value—that is to say, its value at the time of its application to the land—is also largely governed by the mode of " making," and the mode and duration of storage. In virtue of the large quantity of bulky organic or carbonaceous matter that it contains, it improves, by the formation of " humus," the physical condition of the soil, making " heavy " soils more " open," and " light " soils more retentive. At the same time, it returns to the land the mineral matter and much of the nitrogen previously removed from it in the form of straw, as well as much of the nitrogen and most of the phosphoric acid and potash derived from home-grown fodder consumed during its production, reinforced by similar matter derived from the simultaneous consumption of additional purchased food.

The proportion of the nitrogen and mineral matters absorbed and retained by animals from their food depends upon their age, condition and other circumstances. Thus, a young growing steer, or a cow in milk, will assimilate more nitrogen and phosphates, and consequently void less in the form of fæces and urine, than will a fattening ox, which has already built up its frame and principal nitrogenous tissues, and is increasing its weight mainly by the production of fat. Thus the quantity of nitrogen voided in fæces and urine might vary from more than 95% of the nitrogen consumed in the food to as little as 75%. The proportion of phosphoric acid and potash voided will be greater. Obviously, in the case of horses, which spend only a portion of their time in the stable, only a fraction of the excreta will be mingled with the litter; and so also in the case of cattle which are turned out for a part of their time. It is manifestly only the stall-fed or yard-fed animal which contributes the whole of the nitrogen, phosphates, and potash which it voids to the manure heap.

Unfortunately for the farmer, the fertilising matter thus initially contributed to the manure is by no means all ultimately available for utilisation. Continual losses occur. These are at their highest in an open farmyard exposed to the weather, where more or less loss of the valuable soluble constituents of the manure is always going on by mere drainage, and where there is the greatest facility for the evaporation of ammonia. They are at their lowest where the animals are fed in close boxes, in which the litter is trodden down compactly in watertight pits; but even here there is constant loss by reason of fermentative action, not only through evaporation of ammonia, but also by the reduction of ammonia and other easily decomposable nitrogenous compounds into free nitrogen. The losses that thus occur have been studied by numerous investigators, including Lawes and Gilbert, A. Voelcker, J. A. Voelcker, Hall, Maercker and Schneidewind, Holdefleiss, Müntz and Girard, Wood, Russell and numerous others. The general result has been to show that, even under the best conditions of ordinary production, the loss of nitrogen may be expected to amount to about 15% by the time the manure is taken out of the boxes, while in shallow stalls or yards it may amount to 30 or 40%. Further loss of nitrogen takes place after the manure is heaped or stacked for "ripening," or for preservation until it is convenient to transfer it to the land. It is probable that, even with fairly good management, the ultimate loss of nitrogen may amount on the average to 50% of the initial quantity. Under bad management, especially with open yards and free drainage, it is probably often much greater.

Various plans have been adopted or suggested for checking the loss, such as the use of gypsum or superphosphate sprinkled in the manure during its accumulation, to absorb ammonia; or of kainit, which checks fermentation. In any case the manure should be heaped as compactly as possible, with layers of earth in it, and the heap should be covered with earth. It has been demonstrated that the greatest percentage loss of nitrogen unfortunately occurs in the manure that is initially richest, namely, that produced by animals liberally fed on highly nitrogenous food.

It is obviously difficult to give an average composition for so variable a substance as farmyard manure, but broadly it may be said to consist of:

Water	about	75%
Organic and volatile matter .	,,	22%
Mineral matter (exclusive of earth)	,,	2½–3%

But, as the water may vary from perhaps as little as 65% to over 80%, the quantity of organic matter is liable to considerable inverse variation. The proportion of nitrogen is usually from about 0·45–0·65%, that of potash from about 0·4–0·8%, and that of phosphoric acid from about 0·2 to about 0·4%.

Hall ("Fertilisers and Manures," Murray, London, 1929) gives tables illustrating the general composition of farmyard manure, and also showing the influence of feeding on the nitrogen contents of the manure (*see* tables in next column).

Straw manure will contain more potash than peat moss manure, but the latter contains more nitrogen. Stable manure is "hotter"—that is to say, ferments more rapidly—than farmyard manure proper. Very large quantities used to be purchased from town stables by market gardeners and other farmers within easy carriage of cities. But the supersession of horse-traffic by motor-traffic has now diminished this abundant source of fertility to almost a vanishing point. Such manure largely consists of litter that a farmer would regard as only half used, owing to the necessity for the prompt clearing of town stables; and it is necessarily poor in soluble nitrogen compared with farmyard manure. Analyses by Dyer (tabulated by Hall) (see next column) illustrate the composition of specimens of such manure, made both with straw and with peat moss, fresh and after some months' storage in heap on the farm of the purchaser.

COMPOSITION OF FARMYARD MANURE FROM VARIOUS SOURCES (HALL).

—	Water.	Nitrogen.	Phosphoric acid.	Potash.
	%	%	%	%
1. Fresh long-straw manure	66·17	0·544	0·318	0·673
2. No. 1 after rotting .	75·4	0·597	0·454	0·491
3. Very old and short, from a mushroom bed	53·14	0·80	0·63	0·67
4. Fresh } French data	75·0	0·39	0·18	0·45
5. Rotten	75·0	0·50	0·26	0·53
6. Very old	79·0	0·58	0·30	0·50
7. Rothamsted average .	76·0	0·64	0·23	0·32
8. Fresh liquid manure .	98·02	0·044	0·051	0·355
9. Old ditto	99·13	0·026	0·014	0·22

PERCENTAGE COMPOSITION OF FARMYARD MANURE (HALL)

Diet.	Year.	Dry matter.	Total nitrogen.	Nitrogen as ammonia.	Nitrogen as amides.	Insoluble nitrogen.	
Roots and hay only	1904	23·6	0·577	0·046	0·067	0·464	Made into mixen & stored.
Cake-fed	1904	24·03	0·716	0·079	0·096	0·541	
Roots and hay only	1905	29·5	0·462	0·040	0·047	0·375	Do.
Cake-fed	1905	31·3	0·698	0·182	0·055	0·461	
Roots and hay only	1906	22·0	0·466	0·022	0·033	0·411	Do.
Cake-fed	1906	24·3	0·690	0·097	0·049	0·544	
Roots and hay only	1907	25·3	0·589	0·125	0·053	0·411	Not stored.
Cake-fed	1907	25·5	0·815	0·377	0·033	0·405	

In addition to its mineral constituents (phosphates, potash salts, etc.), well-made farmyard manure contains enough available nitrogen in the form of ammonia compounds and easily nitrifiable organic matters to enable it to begin to act as plant food immediately; while it has at the same time a reserve of insoluble matter, partly decomposed organic matter which yields up nitrogen more slowly and gradually, the effect of much of which is realised only in subsequent seasons.

COMPOSITION OF LONDON STABLE MANURE (DYER—TABULATED BY HALL).

—	From peat moss.	From straw.	From mixed peat moss and straw.				
			Fresh.		After storage.		
			1	2	1	2	3
Water . .	77·80	70·0	76·1	62·0	53·8	61·9	52·9
Organic matter	18·00	24·3	19·3	26·4	17·5	22·0	23·0
Nitrogen, sol.	0·51	0·10	0·08	0·08	0·06	0·08	0·10
,, insol.	0·37	0·52	0·46	0·62	0·58	0·68	0·79
Phosphoric acid . .	0·37	0·48	0·33	0·45	0·49	0·56	0·66
Potash . .	1·02	0·59	0·45	0·58	0·58	0·65	0·80

The duration of the action of farmyard manure largely depends upon the nature of the soil. In some "open," "hot," gravelly soils, farmyard manure is used up with remarkable rapidity. On other soils, its action may be spread over a considerable number of years;

but in such cases its fertilising effect especially on arable land, diminishes to an increasing extent each year, until, under the circumstances of ordinary farming, it becomes imperceptible. There are, however, experimental plots at Rothamsted, where, under circumstances peculiarly favourable to its operation, the effects of early dressings of farmyard manure are still evident after the lapse of considerably more than half a century.

The valuation of the unexhausted effect of farmyard manure in relation to the feeding stuffs consumed in producing it, is an important matter in the application of the Agricultural Holdings Act. This subject was fully discussed by Hall and Voelcker in a paper " On the Valuation of the Unexhausted Manure obtained by the Consumption of Foods by Stock," in the Journal of the Royal Agricultural Society of England, 1913, vol. 74 (also republished as a separate pamphlet by John Murray, of Albemarle Street, London, W.). In this paper the original valuation tables of Lawes and Gilbert were revised in the light of later investigation, and, with occasional revision to fit market prices, have been adopted by the Central Association of Tenant-Right Valuers.

The general chemistry of farmyard manure has been well treated by Hall in his work on "Fertilisers and Manures" (Murray, 3rd ed. 1929), and also by Russell and Richards (J. Agric. Sci. 1917, **8**, 495).

There is, however, another effect of farmyard manure which has scarcely yet found its way into text-books. The trend of modern investigation appears to be to indicate that not a little of its value may be due to the stimulating effect on plant growth of relatively minute quantities of organic compounds either contributed directly in the urine of animals or formed subsequently by decomposition. These have received the general descriptive title of *auximones* or *hormones*, though the latter term is less happy since the term " hormones " should, preferably, be restricted to substances produced internally by a living organism for its own needs, rather than extended to include growth-stimulating substances of external acquirement or application. The credit for the first demonstration of the existence and importance of such auximones in decaying organic matters is due to the late Prof. Bottomley of King's College, whose work (1915–17) then failed to receive the attention that it deserved. But of late years the subject has attracted a large number of workers with the result that there is already an extensive literature on the subject. One of the typical substances of this kind is indolyl-acetic acid, and a number of the congeners or analogues of this compound have been found to exhibit similar activity on plant growth. The progress made in this direction up to 1937 was well summarised in a series of papers by Dr. Hugh Nicol, of the Rothamsted Experimental Station, published in " The Manufacturing Chemist " in June, July and August of that year. The subject is too large for discussion here, but it appears desirable to make this brief mention of the fact that investigation now promises to afford scientific justification of the common conviction of the farmer that the manure heap, apart from its mere supply of plant food, possesses some virtues which in the past have lacked adequate scientific explanation (*v.* AUXIN).

It appears, too, not impossible that the presence of auximones or their production during the decomposition of some of the common nitrogenous organic fertilisers may have some bearing on the fact that, for some purposes, farmers, and especially market gardeners, often prefer them, despite the comparative slowness of their action, to inorganic fertilisers of corresponding nitrogen content.

Peruvian Guano. Guano was originally introduced into England from Peru in 1839, and for many years it occupied the first place among concentrated fertilisers. The original rich deposits have been for a long time exhausted, and although occasional importations of fresh rich Peruvian guano have occurred in recent years, most of the fresh deposits are now retained for agricultural use in the country of origin.

Guano is formed from the excrement and carcases of sea-fowl. The fresh excrements are highly nitrogenous, and consist chiefly of uric acid and calcium phosphate. If the climate is hot and dry, the excrements are quickly desiccated and the nitrogenous matter protected. These conditions exist on the rainless coast of Peru. In a moist climate the nitrogenous matter is quickly converted into ammonia and dissipated by evaporation or drainage, a phosphatic guano remaining practically destitute of nitrogen. The main supply of Peruvian guano for 30 years was from the Chincha Islands, which yielded, in all, from what we may call the original deposits, about 10,000,000 tons. This guano was a dry, excellent fertiliser, containing from 13 to 14% of nitrogen, and from 13 to 14% of phosphoric acid. On its exhaustion, about the year 1868, guano was shipped from the Guanape and Macabi Islands. This was a damp guano containing from 9 to 11% of nitrogen, and about 12–14% of phosphoric acid. This was succeeded by importations, still from old deposits, from the Ballesta Islands and the islands of Lobos de Afuera, and deposits on the mainland at Pabellon de Pica, Punta de Lobos, and Huanillos. Many of these deposits were of low nitrogenous content, but rich in phosphates, while some possessed very much the character of the original Chinchas guano.

The nitrogen in Peruvian guano is partly in the form of ammonium salts and partly in organic combination such as urea, uric acid, guanine, etc.; and in some cases small quantities of nitrate are also present. The main part of the phosphoric acid is in the form of finely divided calcium phosphate, some of the phosphoric acid also being in combination with ammonium, sodium or potassium. Part of the phosphoric acid, therefore, is immediately soluble in water, while even that which is insoluble is readily attacked by weak acids and rapidly available as plant food. There is also present an appreciable quantity of potash salts. Guano is, therefore, an extremely valuable manure, and has always commanded relatively higher prices than most other concentrated fertilisers.

Examples of analyses of Peruvian guano of different grades from several of the islands given below, are recorded here although they are now only historically interesting.

	Bal-lestas.	Lobos de Afuera.	Can-tores.	Lobos de Tierra.	South Guanape.	North Guanape.	Lobos de Afuera.		
Moisture . . .	18·06	18·30	28·74	24·44	25·72	16·60	15·20	15·58	10·44
Organic matter and ammonium salts	40·36	36·32	35·66	32·16	29·91	29·50	26·55	19·57	11·96
*Phosphoric acid (P_2O_5) . . .	9·74	10·62	13·25	11·84	14·79	16·35	15·07	17·21	19·13
Lime	9·21	10·53	11·45	10·75	12·25	13·08	12·46	14·17	14·50
†Magnesia, alkalis, etc.	7·93	9·61	9·10	8·64	9·84	11·92	10·65	11·27	12·32
Silicious matter .	14·70	14·62	1·80	12·17	7·49	12·55	20·07	22·20	31·65
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Total nitrogen. .	11·43	9·97	9·44	8·32	7·19	7·07	6·80	4·58	2·58
Equal to ammonia	13·88	12·11	11·46	10·10	8·73	8·58	8·26	5·56	3·13
*Equal to tricalcium phosphate . .	21·28	23·20	28·95	25·87	32·32	35·72	32·93	37·60	41·80
†Including potash .	2·68	2·39	2·76	2·50	2·87	3·09	2·33	2·15	1·86

Besides Peruvian guano, nitrogenous bird guanos of commercial importance have been obtained from Patagonia and from the Ichaboe Islands off the coast of Africa. Ichaboe guano, being from fresh deposits, is rich in nitrogen, of which it contains from 9 to 14%. Its general composition is similar to that of Peruvian guano of similar grade. An appreciable proportion of the nitrogen, however, is in the form of feathers.

Bat Guano.—Large accumulations of this are sometimes found in caves in tropical or sub-tropical regions. Such guano is rich in nitrogen owing to the insectivorous habit of the bats. The deposits often occur in " pockets " and are irregular in composition owing to admixture with earth, and it is rarely that their transport to a distance is commercially profitable. They are best utilised for local fertilisation.

Seaweed.—This is largely used in some localities near the sea. When quite fresh, seaweed contains about 80% of water. Its composition varies a good deal. The nitrogen may be 1–3% of the dry matter. The average percentage of potash in 20 analyses of *Fucus* and *Laminaria* was 3%, and of phosphoric acid 0·5% of the dry matter. The proportion of nitrogen and potash in fresh seaweed is thus very similar to that in farmyard manure, while the phosphoric acid is deficient.

Fish Manure or Fish Guano.—Whole fish are employed as manure in places near the sea. Way found in fresh sprats 63·7% water, 1·94% nitrogen and 2·1% ash, including 0·43 potash and 0·90 phosphoric acid.

Fish manure, or " fish guano," as it is called, is made on a considerable scale from various kinds of fish refuse. The Norwegian fish guano is prepared from cod. Herrings, sprats, menhadden and other oily fish are boiled and pressed for the sake of their oil, and the residue is dried, powdered and sold as fish guano. This manufacture is carried on in various places on the east coast of England and Scotland. It is also carried on to a large extent in London, the raw material being the fish offal of the metropolis, which, for the most part, is simply dried and ground. The principal value of fish guano lies in its nitrogen, which may vary from as little as 6 or 7% to as much as 10 or 11% according to the particular kind of fish or fish offal from which it is made, and the presence or absence of much salt or other impurities. There is also a good deal of calcium phosphate, which may range from as little as 6 or 7% up to 18 or 20%. The potash is inconsiderable. The following analyses represent different qualities of fish guano :—

ANALYSES OF FISH GUANO.

Moisture . .	14·18	8·78	14·42	11·18
*Organic matter	54·07	63·92	63·68	67·22
†Phosphoric acid (P_2O_5) . .	5·58	7·85	7·50	7·72
Lime . . .	6·16	10·47	8·06	8·34
Salt, magnesia, potash, etc. .	17·31	7·03	5·54	5·14
Sand . . .	2·70	1·95	0·80	0·40
	100·00	100·00	100·00	100·00
*Containing nitrogen . . .	6·27	8·74	9·62	10·42
Equal to ammonia . .	7·61	10·61	11·68	12·65
†Calcium phosphate . .	12·19	17·15	16·39	16·87

The modern demand for " fish meal " as an auxiliary feeding stuff for pigs and poultry has, however, largely diminished the quantity of fish residues available for use as fertiliser.

Phosphatic Guanos.—The ancient deposits of guano occurring in climates in which rain is frequent have lost almost the whole of their nitrogenous matter; they are, when free from sand or rock, of value as phosphatic manures, but have been chiefly used for the manufacture of high grade superphosphates. Some of these guanos have been considerably altered by the action of water and other natural chemical agents. One common result of this action is the formation of "crusts," consisting largely of calcium phosphate containing considerably less calcium than tricalcium phosphate, and therefore of special value as manure.

The principal places from which phosphatic guanos have been obtained are various islands in the West Indies and in the Pacific Ocean. Those which more particularly retained some of the distinctive characters of guanos are now for the most part exhausted, and such as are still occasionally obtainable are not imported for direct *use* on the land, but for incorporation in the preparation of "dissolved guanos" or compound fertilisers.

Ammonium Sulphate.—Ammonium sulphate was formerly manufactured almost wholly from gas liquor or coke-oven liquor. At the present time, however, there is a very large output of synthetic ammonia obtained by the direct combination of nitrogen and hydrogen. Simultaneously, the methods of crystallisation and purification of sulphate derived from gas liquor have undergone considerable improvement, especially as regards diminution of free acidity; and there is now an abundant commercial supply of neutral or practically neutral sulphate yielding 21% or more of nitrogen equivalent to from 99-99·5% of pure sulphate. As "neutrality" is often stipulated for, or a limitation of "free acid," an agreed method of testing has been arrived at: 20 g. of the sulphate are dissolved in water, the solution being filtered and made up to 250 c.c., the whole solution being then titrated for acidity, using methyl orange as indicator, the acidity being expressed as H_2SO_4.

Sodium Nitrate (commercially called nitrate of soda) is refined from the crude native deposits (known as caliche), found in the rainless areas of Chile. Good commercial sodium nitrate in its original form contained about 95% of sodium nitrate or 15·6% of nitrogen (equivalent to 19% of ammonia), the impurities being moisture, sodium chloride, sodium and magnesium sulphates, small quantities of iodates and sometimes of potassium perchlorate, while in some cases sodium nitrate is partly replaced by potassium nitrate.

A more refined form, however, is produced by the "Guggenheim" method of extraction from the native caliche. Commercial nitrate thus prepared is now produced containing 98–99% of pure salt in the form of small granules so dry and "easy-running" that cargoes are now shipped in bulk instead of in bags, and discharged by exhaust suction like wheat. Sodium nitrate for use as fertiliser is now also made at Billingham by oxidation of synthetic ammonia to nitric acid and neutralisation with soda.

Potassium Nitrate, or Saltpetre, is sometimes used as a source of both nitrogen and potash, but chiefly in India, where it is a native product.

Calcium Nitrate is also used as a fertiliser. Its chief interest at present lies in the fact that it is manufactured from nitric acid obtained by the catalytic oxidation of ammonia produced synthetically from atmospheric nitrogen (*v.* Vol. I, 332). As put on the market at present, it contains about 15·5% of nitrogen (equivalent to about 19·0% of ammonia). As at present marketed it includes a small admixture of ammonium nitrate, which overcomes the difficulty of the natural deliquescence of the unmixed salt.

Ammonium Nitrate.—Ammonium nitrate is also now extensively used as a fertiliser, not, however, in its unmixed or concentrated form, but intimately mixed with calcium carbonate in which form it is known as "*nitro chalk.*"

Nitro Chalk.—This fertiliser contains 15·5% of total nitrogen of which half is ammoniacal and half nitric nitrogen. It also contains 48% of calcium carbonate, and is granular and therefore easy to sow and well adapted for top dressing.

Calcium Cyanamide is also a fertiliser made from the nitrogen of atmospheric air which is passed through coarsely ground heated calcium carbide. The resulting mass contains a large proportion of calcium cyanamide, and about 18–20% of nitrogen. In moist earth it decomposes, yielding ammonia, according to the reaction $CaCN_2+3H_2O=2NH_3+CaCO_3$; but it is probable that other influences than mere moisture—connected probably with the microbic life of the soil—play a part in the production of ammonia. As calcium carbide is a product of the electric furnace, calcium cyanamide, like calcium nitrate, needs electric power for its production (*v.* CYANAMIDE). It is put on the market under the name of "Kalkstickstoff" on the Continent, or "nitrolim" in England.

Some forms of calcium cyanamide, especially of a granulated type made by using excess of lime, contain considerable quantities of dicyandiamide, the action of which has been alleged to be deleterious to some crops as well as tending to inhibit nitrification in the soil (Voelcker, J. Roy. Agric. Soc. 1917; *also* Cowie, J. Agric. Sci. 1919, **9**, part 2).

More recent investigations (Lefort des Ylouses, Chim. et Ind. 1927, **18**, 216; S. Doldi, Giorn. Chim. Ind. Appl. 1932, **14**, 171; *also* Crowther and Richardson, J. Agric. Sci. 1932, **22**, 301) indicate, however, that dicyandiamide is not in itself directly toxic to crops, but that unsatisfactory field results, following the application of calcium cyanamide or admixtures thereof containing substantial quantities of this derivative, are probably attributable to inhibitive action on nitrifying bacteria.

Calcium cyanamide is now being produced in America in a conveniently finely granulated form in the preparation of which the product is mixed with a substantial quantity of calcium nitrate, with the result that of the 22% of total nitrogen contained in the finished product, about 3% is in the form of nitrate. The effect of this is that the fertiliser is ready to begin its work immediately, independently of the cyclical change of the cyanamide into urea or whatever other compounds precede its ultimate transformation into ammonia and nitrate.

Urea.—Urea has thus far found little use as fertiliser in this country or in America, but in various forms is used as such to a considerable and increasing extent on the Continent of Europe. Urea is obtained in large quantity by the action of various acids on solutions of calcium cyanamide, the action being usually expedited by some catalyst, such as manganese dioxide or other suitable metallic oxide. (Carbon dioxide and manganese dioxide, Akt.-Ges. für Stickstoffdünger, G.P. 301262, 22/3/16; sulphuric acid and manganese dioxide, Meister, Lucius and Brüning, G.P. 311018, 14/3/16, and 311019, 17/3/16; sulphuric acid and ferroso-ferric-oxide, M. L. & B., G.P. 301278, 17/3/16; nitric acid and calcium nitrate, Nydegger and Schellenburg, B.P. 153574, 25/10/20; mineral acids under pressure, *e.g.* 5 atms. at 75°C., Soc. d'Études Chim. pour l'Ind., B.P. 192703, 1/2/23.) Commercially purified urea, containing 46% of nitrogen, is listed abroad among nitrogenous fertilisers, but would seem to be too concentrated for direct use owing to the difficulties of equable distribution in the field. It is also commercially supplied in the form of urea nitrate, which contains 34% of nitrogen. The most popular and most convenient form, however, in which it is supplied to the agriculturist is what appears to be a molecular combination of calcium nitrate and urea, in the proportion of one equivalent of calcium nitrate to four equivalents of urea. This affords a stable combination resulting in an article containing about the same proportion of nitrogen (34%) as is yielded by urea nitrate. It is obtained by dissolving calcium nitrate in a solution of urea in the molecular proportions indicated, the solution being concentrated by heat until a " melt " is obtained containing only insignificant quantities of water, and then converted into granulated form by a process of spraying (Badische Anilin- u. Soda-Fabrik., B.P. 246377, 22/6/25; and I.G. Farbenind. A.-G., B.P. 332945 and 332948 both of 29/4/29).

Oilcakes.—Cheap or damaged oilcakes, or cakes unfit for food (as castor), are employed to a considerable extent as manure, and more particularly the residual meals obtained as by-products in the extraction of oil by volatile solvents from rape seeds, castor-oil seed and numerous other oil seeds. They are in request for hop manuring, and for general use on light soils, on which the farmer prefers a less rapidly active form of nitrogen than is furnished by guano, sodium nitrate or ammonium sulphate. They may contain 4–7% of nitrogen, 1·5–3·0% phosphoric anhydride and 1–2% potash.

Hoof and Horn.—The powdered horn obtained in making combs and other articles is used to a considerable extent by manure manufacturers; it is rich in nitrogen, containing about 15%.

Crushed hoof and horns in coarse form are also in considerable demand by hop-growers and market gardeners as yielding during decomposition a slow but steady supply of available nitrogen.

Dried Blood.—This is a very valuable manure, its nitrogenous matter becoming available to the crop soon after mixing with the soil. Perfectly dry blood will contain about 15% nitrogen and 4% ash, of which one-half is common salt. The commercial article contains from about 11–14% of nitrogen. It is in growing demand for direct application to the soil, but the greater part both of the dried blood manufactured here and of that imported from South America is purchased by the manure makers and incorporated in compound fertilisers.

Meat meal, Meat Guano.—The residue from the manufacture of meat extract is exported as manure from South America, and from Queensland and New Zealand. The composition varies much, chiefly according to the proportion of bone ground up with the meat. The nitrogenous samples may contain 11–13% nitrogen, and 0·6–3·0% phosphoric anhydride. The phosphatic samples may contain 6–7% nitrogen, and 14–17% phosphoric acid. The better grades of meat meal, however, are now in demand as feeding stuffs for farm stock.

Shoddy and Wool Waste.—These are useful nitrogenous manures, but less active than those previously enumerated, being only slowly decomposed in the soil. They are used mainly for hops and in market gardening. Pure dry wool and hair would contain about 17% nitrogen and 2% ash. The percentage of nitrogen in ordinary shoddy varies from about 5 to 8, the general average being about 7. Shoddy is apt to contain a good deal of water; the other impurities are cotton waste and mineral matter.

Leather.—The percentage of nitrogen is 4–6. This is the least active form of nitrogenous matter used as manure; but there are various manufacturing processes—such as treatment with acids or with steam under high pressure—whereby the distinctive character of the leather is more or less destroyed, the result being a fine powder capable of undergoing more rapid decomposition.

Soot.—House soot is used by farmers as a top dressing for spring corn. Good soot contains about 4% of nitrogen or nearly 5% of ammonia (say 20% of ammonium sulphate, in which form the nitrogen largely exists), but it often contains an admixture of ashes, and consequently varies a good deal in strength. When used in large quantities the carbon is believed to improve the mechanical condition of clay soils, and its temporary darkening of the surface tint of pale coloured clay land is said to be of value in conserving for the time being an appreciably higher degree of temperature in the surface soil by diminishing radiation.

Bones.—These are seldom used in their fresh state; they have generally been first steamed to extract the fat. The extraction of fat by organic solvents is also in practice. This results in less loss of nitrogen than does the steaming process. A third form of bone is that left after extracting the greater part of the gelatinous matter by boiling under pressure. The analyses shown at the top of the next page illustrate the composition of bone manures.

Bones are either applied to the land directly as crushed bones, or as bone-dust or bone-flour; or they are employed for the manufacture of " dissolved bone." The soft parts of bone are more nitrogenous than the hard parts. Bone-

BONE MEAL.

	English (containing cartilaginous matter).	English (ordinary).	Indian.	Boiled or lightly steamed.	De-gelatinised bone-flour.
Moisture .	8·24	8·80	8·48	8·62	13·52
*Organic matter .	36·14	34·94	30·56	20·74	9·88
†Phosphoric acid .	20·75	21·66	24·19	26·44	30·11
Lime . .	27·94	28·53	32·03	35·95	40·04
Magnesia, carbonic acid, etc.	5·18	4·62	4·19	7·25	5·45
Silicious matter .	1·75	1·45	0·55	1·00	1·00
	100·00	100·00	100·00	100·00	100·00
*Containing nitrogen	4·72	4·19	40·1	2·33	0·91
Equal to ammonia	5·73	5·09	4·87	2·83	1·11
†Equal to tricalcium phosphate	45·34	47·33	52·85	57·77	65·79

flour is a fine powder, prepared from highly steamed bones.

Bone Ash was formerly much used for preparing high-class superphosphates, but is now rarely used, owing to the abundance of cheaper phosphates. The commercial article, such as was formerly imported in large quantities from South America, contained from 75 to 80% of tricalcium phosphate.

Basic Slag.—By the process patented by Thomas (1877–79), the phosphorus is removed from pig-iron. To molten iron in a Bessemer converter lined with lime, a large dose of lime is added, and the blast applied. At the high temperature reached, the impurities in the iron are oxidised by the air introduced, the phosphorus becomes phosphorus pentoxide and unites with the lime. A slag is formed containing about 40–50% lime, varying quantities of magnesia, alumina, iron oxide, manganese oxide, silica and phosphoric acid equivalent to from 20 to 50% of tricalcium phosphate. Basic slag is now an important product of the iron and steel industry.

For several years the slag was regarded as valueless, the large amount of iron present leading to a presumption that its phosphoric acid would not prove available to plants, while the ferrous oxide would probably be injurious. It was, however, found that the phosphoric acid in the slag is almost wholly combined with calcium, and that this calcium phosphate is easily disintegrated and rendered soluble in the soil, and that no ill effects arise from the presence of ferrous oxide. Tetracalcium phosphate has been suggested as the combination in which most of the phosphorus occurs, but it is now regarded as probable that the phosphate has more nearly the composition $(CaO)_5,P_2O_5SiO_2$. The phosphate in the slag is not soluble in water; it is dissolved to a considerable extent by a solution of ammonium citrate, and when the slag is finely ground about 80% of it should dissolve in a 2% solution of citric acid.

Much basic slag, however, is produced in the open hearth process. This is of lower grade of phosphorus content and of low citric acid-solubility owing to the use of calcium fluoride as a flux. It is now generally conceded on the result of experimental trials that the practical value of basic slag is very largely dependent upon the degree of citric acid-solubility of the phosphoric acid. The use of calcium fluoride as a flux (resulting in the conversion of some of the phosphorus into artificial apatite, which is not thus soluble) is a disadvantage from the point of view of the fertilising effect of the slag.

To be effective the slag must be finely ground; at least 80% of it should pass through a sieve having 100 meshes to the linear inch. The grinding requires special machinery. It is advisable, according to Horn (J.S.C.I. 1886, **5**, 242), to break first under stamps, to further reduce between rollers, then to separate pieces of iron by passing over slanting sieves, and finally to grind between millstones.

Basic slag is especially valuable on moorland soils rich in organic matter and on clay soils deficient in lime on which the continuous use of superphosphate is undesirable. It has proved especially valuable on pasture land on which it encourages the growth of white clover.

Precipitated Phosphate. — Phosphatic minerals which are unsuitable for the manufacture of superphosphate, either from their poverty in phosphate or from the presence of an objectionable amount of iron oxide or alumina, are sometimes treated with acid, the calcium phosphate dissolved out, and then recovered by precipitation. If the addition of the neutralising base is stopped while the solution is still acid, the precipitate will consist chiefly of dicalcium phosphate.

The phosphoric acid in precipitated phosphate stands next in value to that existing as monocalcium phosphate. Commercial dicalcium phosphate may contain as much as 40% P_2O_5 and is thus a very concentrated fertiliser. Since the introduction of basic slag, however, it is now scarcely worth while to manufacture precipitated phosphate except as a by-product. It is thus prepared incidentally to the manufacture of gelatin from bones. The bones are treated with cold hydrochloric acid, which dissolves out the phosphate, leaving the gelatinoid matter undissolved. The phosphate is then recovered from the acid solution by precipitation with milk of lime.

Rhenania Phosphate.—This is an artificial preparation made by igniting raw mineral phosphatic rock with silica and subsequently grinding to fine-meal. The phosphoric acid is mainly converted into a form soluble in alkaline ammonium citrate (Petermann). The finished article contains as much as 27% of "citrate-soluble" phosphoric acid.

Superphosphate.—Some of the natural mineral phosphates may be applied directly to the soil with good effect, if in the condition of sufficiently fine powder. Many of the natural mineral phosphatic deposits are, however, too hard and insoluble to be economically used in this manner, and must be treated with sulphuric acid and converted into superphosphate.

The treatment of bone with sulphuric acid was originally recommended by Liebig. The treatment of mineral phosphates with sulphuric acid originated with Lawes, who took out a patent for this process in 1842, and founded a manufacture which has since reached enormous dimensions. A statistical report of the International Superphosphate Manufacturers' Association for 1937 estimated the world's production of superphosphate for that year at nearly seventeen million tons.

Superphosphate in the United Kingdom is now sold on the basis of its percentage of water-soluble phosphoric acid (P_2O_5). Formerly it was sold on the percentage of "soluble phosphate"—which term indicated the quantity of original tricalcium phosphate to which the water-soluble P_2O_5 was equivalent. The term is still sometimes used, but the Fertilisers and Feeding Stuffs Act, 1926, now in force, requires the vendor to give his guarantee in terms of P_2O_5.

PHOSPHATE MATERIALS USED.—Superphosphate was prepared by Lawes in the first instance from spent animal charcoal; Suffolk (Tertiary) coprolite and Estremadura phosphorite were also early employed. The Suffolk coprolite was for 15 years the principal material made use of. The far superior Cambridge (Greensand) coprolite then became for many years the chief material, but these coprolites are no longer used. Deposits rich in calcium phosphate have been found all over the world; many of these have been exhausted, and others given up as of inferior quality, or as being at present prices too expensive to work. The following account is given however both of some of those which have become matters of history, or the use of which is at present in abeyance from the effect of competition, as well as of those which are at present in use.

SOUTH CAROLINA OR CHARLESTON PHOSPHATE.—This is apparently a converted Eocene marl, occurring in rough masses, largely perforated by boring mollusca, and associated with fossil bones and teeth. It is classed as "land" and "river" phosphate; the latter is obtained by dredging the Bull, Coosaw and Stono rivers. This phosphate came first into use in 1867, and soon became the chief material for the manufacture of superphosphate. The quantity exported to the United Kingdom in 1887 was 165,275 tons (principally river phosphate); in the same year 430,549 tons were used in the United States. There are three grades, containing phosphoric acid equal to 50–52, 55–56 and 58–60% tricalcium phosphate; they differ mainly in the proportion of silicious matter present. South Carolina phosphate, though not rich enough for the preparation of high-class superphosphates, was an admirable material for the production of an ordinary superphosphate, containing, according to the quality of the phosphate used, from 11 to 14% soluble phosphoric acid, or, in commercial language, 24–30% soluble phosphate. But, owing to the discovery of other deposits and to the local demand for this particular phosphate in the United States, it has at present practically ceased to be imported into England.

BELGIAN AND SOMME PHOSPHATE.—In the north of France (departments Somme and Pas de Calais) and in the adjoining districts of Belgium there exists a large deposit of a friable phosphatic rock, "craie grise," extending over seven million acres. This deposit lies on ordinary white chalk; it consists of yellowish grains embedded in a chalky matrix. The rock contains 20–30% of calcium phosphate, occurring in the crystalline grains above mentioned. In the upper layer of this deposit are pockets, chiefly developed in the French area, which contain a sand richer in phosphate and poorer in carbonate than the underlying rock, the proportion of phosphate in this sand being 50–80%. The sand has probably been formed from the original rock by the action of water. This phosphatic sand is known as "Somme phosphate."

The Belgian phosphatic rock is generally of low quality. By washing and blowing, a material containing 40–45% calcium phosphate is produced. Many schemes have been tried for removing the calcium carbonate, and thus raising the value of the material; none has yet become a commercial success. Belgian phosphate has been much used with other phosphates as a diluent; the carbonate it contains produces much gypsum when acted on by the sulphuric acid, and considerably improves the porosity and dryness of the manure. These phosphates are now little, if at all, used in England.

PHOSPHORITES.—Large deposits of apatite, or of phosphates having an apatite character, occur in many places; those most worked have been the Estremadura, the Canadian and the Norwegian. These, however, are not now brought to this country, and have for the present ceased to be worked, but Russian apatite (under the name of "Kola phosphate"), concentrated by a levigation process, is being produced in considerable quantity, and is in use on the Continent for the production of superphosphate.

1. *Estremadura Phosphorite.*—An immense deposit occurs in Caceres. In composition it is a fluor-apatite, but mixed with much quartz, and with more or less calcium carbonate. There are three qualities, containing about 50, 60 and 70% tricalcium phosphate. The calcium carbonate varies from 6 to 16%. The exports were in former years large, amounting sometimes to 60,000 tons per annum, but it has long ceased to be used in England.

2. *Canadian Phosphorite.*—This is much richer than the Estremadura phosphorite, containing 70–80% tricalcium phosphate. The lower qualities contain much mica. The amount formerly exported to the United Kingdom was considerable, but it is not now in use here.

3. *Russian ("Kola") Phosphate.*—This in the "concentrated" form in which it is marketed, contains about 38–39% of phosphoric acid equivalent to 83–85% of tricalcium phosphate. Samples analysed by the writer have been found to contain 0·85–1·0% of iron oxide, about 0·4–0·6% of alumina and about 0·8% of titanium oxide.

CARIBBEAN PHOSPHATES.—Under this head are grouped the rock phosphates found on many of the West India Islands, some of which are often classed as phosphatic guanos.

1. *Aruba.*—This is one of the Dutch islands. The phosphate is of high quality, containing 75–80% tricalcium phosphate, but imports here have long ceased.

2. *Curaçao.*—Another Dutch island. This, which is still being largely worked and is one of the finest phosphates available, contains about 78–85% tricalcium phosphate. It is used to a large extent in making high-grade superphosphate, mainly in Continental fertiliser factories.

3. *Sombrero.*—This valuable deposit, now exhausted, contained 70–75% tricalcium phosphate.

4. *Navassa.*—This contained the equivalent to 60–70% tricalcium phosphate, but too much iron oxide and alumina. It is now rarely heard of.

Bordeaux Phosphate.—Raised in the departments of Lot and Tarn-et-Garonne. This is now little used in England, as it is not rich in phosphate, and contains much ferric oxide and alumina.

Nassau or Lahn Phosphate.—This is still used locally, but the exports to this country have ceased. It varies much in composition; the higher qualities are suitable for the manufacture of superphosphate, but the lower qualities contain much iron. This phosphate is remarkable as containing a distinct amount of iodine.

Coprolites.—The phosphatic nodules commonly known as coprolites, found in England, are no longer in use. The Cambridge (Upper Greensand) coprolite was the best of the English sorts; it contained 55–60% tricalcium phosphate, without an admixture of ingredients prejudicial to the production of soluble phosphate. The Suffolk coprolite (Tertiary) contained less phosphate (55%) and more ferric oxide. The Bedfordshire coprolite (Lower Greensand) was still more inferior, the ferric oxide being present in increased proportion. But these various coprolites possess a permanent historical interest, as being the original form of phosphate used by Lawes for the production of superphosphate.

In France there are considerable deposits of coprolite in the Upper Greensand in the departments of Pas de Calais, Meuse and Ardennes. These generally contain a low proportion of phosphate, and much silicious matter.

Florida Phosphate.—Extensive deposits of high-grade phosphate have been opened up during later years in the State of Florida. The phosphate is of two kinds, namely, " hard rock " phosphate and " pebble " phosphate. The rock phosphate commonly contains from 78 to 80% of tricalcium phosphate, and the pebble phosphate about 70–74%. There is, however, also a high-grade pebble phosphate containing from 78 to 79% of tricalcium phosphate. These phosphates are very widely used for superphosphate.

African Phosphate.—An extensive range of phosphate deposits exists on or near the northern coast of Africa, known in commerce as Algerian, Tunisian, Tocqueville, Gafsa and Egyptian phosphates. These are soft, powdery or friable minerals, containing for the most part comparatively little silicious matter, but a large proportion of calcium carbonate. The proportion of tricalcium phosphate commonly approximates to 60%, varying from about 59% to nearly 64%.

Christmas Island Phosphate.—This is a deposit found on Christmas Island—an island lying in the Indian Ocean south of Java. It contains about 87% of tricalcium phosphate, and makes excellent superphosphate. At present the output is said to be largely consumed in the manufacture of superphosphate in Japan.

Pacific Phosphate.—Valuable deposits of similar high-grade phosphates, containing 86 or 87% of tricalcium phosphate, accompanied by very little ferric oxide or alumina and practically no silica, occur on certain islands in the Pacific Ocean lying to the north-east of Australia. The principal deposits at present worked are those of Ocean Island and Nauru Island, but deposits have also been found on the islands of Makatea, Tahiti and Angaur. Much of the phosphate raised on these islands is consumed for superphosphate making in Australia, New Zealand and Japan.

The world output of mineral phosphate from all sources during the year 1937, as statistically compiled by the Phosphate Export Association of New York and London, was approximately 12,000,000 tons. Of this output 469,227 tons were imported into the United Kingdom, being as follows :—

	Metric tons.
Florida (Pebble)	5,576
Algerian (Constantine)	85,366
Tunisian :	
Gafsa	166,558
Tunisia	28,946
M'dilla	77,438
Morocco	88,130
Ocean-Nauru	5,817
Russia	10,896
France	500
	469,227

Ground Mineral Phosphates.—Owing to improvements in milling machinery available for fine grinding in recent years, much development has occurred in the direct application to the soil of the softer types of mineral phosphate, notably those found in various parts of North Africa. For direct use on the land, these are usually ground so finely that from 80–90% of the powder passes through a sieve having 120 meshes I.M.M. per linear inch. These phosphates have a range of from about 25–32% of phosphoric acid (P_2O_5), say 55–69% of tricalcium phosphate, calculated on dry basis. They appear to answer well on some soils where climatic conditions are favourable but, where early results are looked for, the application of phosphoric acid in this form needs to be larger than when the phosphate is first rendered soluble as in superphosphate. " Hard " phosphates, especially those of the apatite form, are unsuitable for direct application to the soil, however finely ground.

Manufacture of Superphosphate.—The raw phosphate is first reduced to an extremely fine powder. If the material is in large lumps, it is first reduced by means of a crusher, and is then transferred to a suitable mill. The Kent mill is largely used for this purpose, and is worked in conjunction with a screen and elevator. The finer the powder obtained, the more complete will be the decomposition by the sulphuric acid. For first-class work the powder should pass through a sieve of 80 wires to the inch. In view of the stringency of modern factory legislation, a dust-collecting plant of some sort, such as the Beth filter, is usually considered necessary in the part of the works devoted to milling.

It has been assumed in some text-books that the reaction in superphosphate making is simply

$$Ca_3P_2O_8+2H_2SO_4=CaH_4P_2O_8+2CaSO_4.$$

This may be true as regards the major portion

PERCENTAGE COMPOSITION OF MINERAL PHOSPHATES EMPLOYED IN THE MANUFACTURE OF SUPERPHOSPHATE.

(From analyses made by the writer of this article.)

FLORIDA PHOSPHATES. (Dried at 100°.)

	Hard rock.			Pebble, medium grade.				Pebble, high grade.	
*Phosphoric acid (P_2O_5) . . .	36·05	36·44	36·81	31·92	32·24	32·80	33·98	36·24	35·90
Lime	51·29	50·46	50·96	46·76	46·78	47·18	48·03	49·44	48·68
Alumina . . .	1·42	1·44	1·41	1·28	1·29	1·32	1·23	1·32	9·20
Ferric oxide (exclusive of any pyrites) . . .	0·60	0·60	0·55	1·45	1·50	1·85	1·05	0·60	
Magnesia, carbonic acid, fluorine, etc.	7·84	6·31	6·67	11·66	10·43	9·50	9·46	6·40	
Silicious matter .	2·80	4·75	3·60	6·93	7·76	7·35	6·25	6·00	6·22
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
*Equal to tricalcium phosphate . .	78·77	79·62	80·43	69·75	70·44	71·67	74·25	79·18	78·44
Excess of lime over tricalcium phosphate . . .	8·57	7·28	7·34	8·93	8·58	8·31	7·76	6·50	6·14
Moisture in phosphate as imported . . .	0·66	1·60	—	2·11	1·94	2·03	2·33	—	—

NORTH AFRICAN PHOSPHATES. (Dried at 100°.)

	Algerian.		Tocqueville.	Tunisian.		Gafsa.	Kalaa Djerda.	Kosseir.	Morocco.
*Phosphoric acid (P_2O_5) . . .	27·05	29·04	25·26	27·21	28·44	27·12	27·68	32·89	34·55
Lime	47·79	50·46	43·01	48·83	49·92	44·87	49·60	49·75	52·48
Alumina . . .	0·56	0·44	0·52	0·54	0·48	0·96	0·47	0·38	0·70
Ferric oxide (exclusive of any pyrites) . . .	0·25	0·30	0·48	0·30	0·25	0·40	0·30	0·60	
Magnesia, carbonic acid, fluorine, etc.	18·95	16·96	17·33	17·66	17·41	18·95	18·85	13·34	11·17
Silicious matter .	5·40	2·80	13·40	5·46	3·50	7·70	3·10	3·04	1·10
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
*Equal to tricalcium phosphate . .	59·10	63·45	55·19	59·45	62·14	59·26	60·45	71·79	75·49
Excess of lime over tricalcium phosphate . . .	15·74	16·05	13·08	16·59	16·22	12·73	16·83	10·85	11·54
Moisture in phosphate as imported . . .	—	—	—	3·30	3·24	—	4·06	2·15	2·52

VARIOUS PHOSPHATES.

(Dried at 100°.)

	Christmas Island.	Ocean-Nauru.	Tennessee.	Belgian.	French.	Canadian.	
						Rich.	Poor.
*Phosphoric acid (P_2O_5)	39·85	39·84	36·92	19·57	23·80	39·32	29·99
Lime	52·24	53·05	50·59	49·34	52·96	54·18	42·25
Alumina	1·35	0·30	1·59	0·43	1·44	0·40	2·84
Ferric oxide (exclusive of any pyrites)	0·45	0·23	1·70	0·65	0·60	0·55	2·03
Magnesia, carbonic acid, fluorine, etc.	5·96	6·48	7·46	26·23	20·60	4·11	9·27
Silicious matter	0·15	0·10	1·74	3·78	0·60	1·44	13·62
	100·00	100·00	100·00	100·00	100·00	100·00	100·00
*Equal to tricalcium phosphate	87·07	87·05	80·60	42·76	52·00	85·84	65·47
Excess of lime over tricalcium phosphate	5·02	5·84	6·91	26·15	24·76	7·66	6·77
Moisture in phosphate as imported	1·54	2·52	1·21	0·45	—	—	4·8[illegible]

	Spanish.		West Indian.		Coprolites.		South Carolina.
	High grade.	Poor.	Aruba.	Curaçao.	Bedfordshire.	Suffolk.	
*Phosphoric acid (P_2O_5)	35·01	25·77	33·63	37·00	25·97	26·30	26·73
Lime	48·49	34·58	48·33	51·55	40·66	41·72	43·62
Alumina	1·79	7·10	1·63	0·20	1·48	22·90	0·83
Ferric oxide (exclusive of any pyrites)	1·05		1·75	0·24	5·30		1·45
Magnesia, carbonic acid, fluorine, etc.	7·98		12·10	10·90	14·03		17·77
Silicious matter	5·68	32·55	2·56	0·10	12·56	9·08	9·60
	100·00	100·00	100·00	100·00	100·00	100·00	100·00
*Equal to tricalcium phosphate	76·43	56·26	73·48	80·81	56·69	57·42	58·35
Excess of lime over tricalcium phosphate	7·07	4·09	8·48	7·00	9·94	10·60	12·00
Moisture in phosphate as imported	—	1·17	3·04	2·00	0·65	1·41	0·90

of the phosphate rendered soluble. But in practice, as was first pointed out by Ruffle (J.S.C.I. 1887, **6**, 327), the reaction, as regards an appreciable portion of the phosphate, almost invariably proceeds further, thus:

$$Ca_3P_2O_8+3H_2SO_4=2H_3PO_4+3CaSO_4$$

so that a water solution of superphosphate contains a major proportion of $CaH_4P_2O_8$, with a minor proportion of free phosphoric acid H_3PO_4. Indeed, unless there is a fair proportion of the latter, the "soluble" phosphate is unstable, owing to liability to reversion by subsequent interaction between the dissolved phosphate and that which was originally left undissolved. Thus superphosphate, when freshly made, may contain as much as from 6 to 10% of H_3PO_4, and sometimes more.

In the first stage of the reaction, probably phosphoric acid alone is produced, and this afterwards reacts on the remaining undecomposed phosphate. The proportion of free phosphoric acid in the resulting manure is greater when strong sulphuric acid has been employed, the total soluble phosphoric acid being, at the same time, diminished. When superphosphates are dried at 100°, a loss of soluble phosphoric acid also occurs, and this loss becomes greater when a higher temperature is employed (Ruffle).

A further reaction which is of some practical moment to the manufacturer of superphosphate is the diminution of soluble phosphate by keeping. The regenerated insoluble phosphate is known as "reverted phosphate." This deterioration during storage is not observed in the case of well-made superphosphate prepared from finely ground mineral phosphate containing only an insignificant quantity of iron or aluminium, but it occurs when ferric oxide or alumina is present in any considerable quantity.

So long as superphosphate is valued only on the basis of its content of water-soluble phosphate, ferruginous and aluminous phosphates will be avoided by the manufacturer. On the Continent, however, and in the United States, reverted phosphate has a considerable money value, allowing of the use of mineral phosphates containing relatively large quantities of iron and aluminium.

The sulphuric acid employed is usually pyrites-made chamber acid of 1·55 to 1·60 sp.gr. Weak acid is essential, as the dryness of the superphosphate depends largely upon sufficient water being present for the crystallisation of the calcium sulphate ($CaSO_4,2H_2O$) formed by the reaction. It follows that, when much calcium carbonate is present in the phosphate, weaker acid will be required than when but little calcium carbonate is present. When calcium fluoride is present in considerable quantity, and very little or no calcium carbonate (as in apatite), acid stronger even than 1·66 sp.gr. is necessary, as calcium fluoride is not so readily decomposed as calcium carbonate.

The proportion of sulphuric acid to be used depends, of course, upon the composition of the phosphatic material. Theoretically, 100 of tricalcium phosphate will require 94 of sulphuric acid of sp.gr. 1·60 (55% SO_3), or 100 of sulphuric acid of sp.gr. 1·55 (51·5% SO_3), if monocalcium phosphate is to be produced. The proportion of sulphuric acid used in practice is usually as large as can be employed without endangering the dryness of the product. It is generally somewhat in excess of that needed to produce monocalcium phosphate, but is considerably below that required to yield only phosphoric acid.

The excess of lime present in the phosphate (as carbonate or fluoride) is a principal factor in determining the quantity of sulphuric acid to be employed: 100 of lime will require 260 of acid sp.gr. 1·6 or 277 of acid sp.gr. 1·55 to produce calcium sulphate. At the foot of the tables previously given will be found the excess of lime (over that required to form tricalcium phosphate) present in each of the mineral phosphates commonly employed. Phosphates containing a considerable excess of lime will obviously yield a poorer superphosphate than their percentage of phosphoric acid would seem to indicate, owing to the large proportion of sulphuric acid which they require.

In the earlier methods of manufacture of superphosphate, the powdered phosphate was poured into the mixer from bags while a measured quantity of acid was run in from a tank, the mixer consisting of a cylinder containing a revolving shaft with arms or paddles, the contents, after a brief mixing, being discharged by a valve into a pit or "den" in which it was hardened, and from which it was subsequently excavated originally by hand labour, but later by suitable mechanical means.

Of recent years, however, considerable improvements of a mechanical nature have been made in the manufacture of superphosphate with the result that the superphosphate now produced is much drier and more granular than the earlier forms, and no longer exhibits the troublesome tendency to cake and clog the drills or other mechanical devices used for distributing it on the land—a very great practical advantage.

In one form of modern plant (known as the "Broadfield" plant), the finely ground raw phosphate and the acid are continuously fed together in proper proportions into a mixer supplied with paddles by which the mixture is agitated from 4–5 minutes, being continuously discharged into a den having the form of a horizontal cylinder in which it "sets" or solidifies. This cylindrical den contains a travelling "carriage" on which is mounted a cutter, the motion of the carriage and that of the cutter being effected by an electric motor. The "carriage" travels along the den, while the cutter reduces to powder the mass of superphosphate in front of it, and this is finally discharged by means of belt conveyers into the storage bin. This form of den is known as the "Wenk" den. There is, however, another form of den (known as the "Milch" den) which is planned in the reverse sense, the den itself (a steel cylinder) being mounted on wheels so that it travels forward on to a fixed "excavator," on which is mounted a cutting apparatus similar to that on the movable carriage used in the "Wenk" den.

A new mode of manufacture, which is also in use in England, has been patented by Messrs. Ober & Sons of Maryland, B.P. 357508, 357509, 358529, all of 1931. The plant used, which is necessarily more complicated than that in earlier modes of manufacture, is so contrived that a stream of acid passes to a "receiving zone" where it meets and intermixes with a stream of mineral phosphate in a state of fine division, the combined stream being passed under pressure into a horizontal cylindrical autoclave which is kept in continual rotation, and has an outer jacket by means of which its temperature may be raised or lowered. The mixture of phosphate powder and acid is drawn into the autoclave by aid of a partial vacuum until a full charge has been introduced, when the exhaust is closed and the charge is allowed to produce under pressure of its own reaction the gases and vapours generated by the chemical reactions which are going on. The full internal pressure thus set up is maintained for a time and then released, the escaping gases and vapours being passed through a condenser. The result of the release and expansion of gases and vapours causes a sudden drop in the temperature of the contents of the autoclave, which may be further reduced by admitting a "cooling medium" into the hollow jacket of the autoclave. It is claimed that the sudden drop in temperature accelerates crystallisation.

Subsequently, the superphosphate is dried by replacing the "cooling medium" in the jacket of the autoclave by a "heating medium," while simultaneously the autoclave is subjected to partial atmospheric evacuation by means of an exhaust, with the result that the contents are rapidly dried. During the whole of the process the contents of the autoclave are being agitated by the constant maintenance of the rotary motion of the autoclave. The superphosphate, which is then in a well dried and powdery condition, needing no further attrition, is removed from the autoclave in the state ready for storage or transport. The plant is diagrammatically shown in detail in the drawing attached to B.P. 357508 (September 7th, 1931).

In whatever process used, the gases given off during the reaction, both from the mixer and pit, are of a particularly unpleasant description, especially when the phosphate contains fluorides. Both mixer and pit are provided with flues in connection with a fan, by which all the gases are removed; these are purified in a scrubber, and then conducted to a tall chimney.

For many years the favourite type of superphosphate was one containing about 12% of soluble phosphoric acid (equivalent to 26–28% of tricalcium phosphate), but this grade has now been largely replaced by a grade containing about 13·7% of phosphoric acid (equivalent to 30% of tricalcium phosphate), and by a higher grade having from 16–17% of phosphoric acid (equivalent to 35–37% of tricalcium phosphate). Higher grades still are common and continue to be manufactured, especially for export purposes to economise freight, and for use in making compound fertilisers.

Far richer superphosphates are obtained by the process patented by Packard (B.P. 6176, 6750, 6751, 6752, all of 1884). Superphosphate, prepared so as to be rich in free phosphoric acid, is extracted with water, the solution evaporated to sp.gr. 1·125–1·300, and sufficient calcium phosphate, carbonate or hydroxide added to leave one-third of the phosphoric acid in the free state. The solution is then filtered, and the filtrate evaporated to dryness. The product contains about 40% of soluble phosphoric acid, equal to 87% of so-called " soluble phosphate." This superphosphate has a special value where manure has to be conveyed a long distance.

" Dissolved " or " Vitriolised " Bones.—Owing to the requirements of the Fertilisers and Feeding Stuffs Act, the term " dissolved bone " or " vitriolised bone " is restricted to fertilisers made from pure bone and acid only. Usually, in such cases, only from one-half to two-thirds of the phosphate is actually soluble in water, but much of the remainder is in the readily assimilable form of dicalcium dihydrogen phosphate. If enough acid were used to dissolve all the phosphate, the product would be too pasty for sowing.

A lower grade of fertiliser known as " Dissolved Bone Compound " is made by adding to the mineral phosphate, prior to the addition of acid, a variable quantity of bone-meal together with small quantities of dried blood or other nitrogenous material.

Mixed or Compound Fertilisers.—Special fertilising mixtures designed for different crops have been provided by leading manufacturers of chemical manures ever since the early days of superphosphate manufacture. Such mixtures usually consist of superphosphate with ammonium sulphate and salts of potassium, with, in some cases, the inclusion of sodium or potassium nitrate, organic nitrogenous fertilisers, bone meal, etc., in proportions varying with the purpose for which the fertilisers are intended, with a view to relieving the farmer from the more troublesome, though sometimes more economic, alternative of purchasing the simpler fertilisers separately and mixing them for himself. In some of these compound fertilisers other organic nitrogenous ingredients —such as dried blood, hoof and horn meal or leather meal—are mixed with the mineral phosphate before its conversion into superphosphate by admixture with sulphuric acid, ammonium sulphate and potash salts being subsequently mixed in.

Later developments, however, have occurred in the preparation of compound fertilisers whereby, instead of mere dry mixtures of superphosphate, potassium salts, ammonium salts, etc., soluble phosphoric acid is furnished in the form of ammonium phosphate or potassium phosphate or both. These salts may be blended with ammonium or potassium sulphate, yielding a granular form of which every fragment contains its proper fractional proportion of each fertilising element with the advantage that all are distributed, not only simultaneously, but with a regularity less easily obtainable with the more old-fashioned mixtures.

In England, these compounds are prepared on a considerable scale at Billingham where is produced synthetic ammonia and this, combined with phosphoric acid, makes an ammonium phosphate which is mixed in various proportions with ammonium sulphate and potassium sulphate, the mixture, by a process of wetting and drying and the use of appropriate machinery, being converted into a uniform granular condition. In some cases suitable forms of " insoluble " calcium phosphate are also introduced into the mixture.

Thus a series of fertilisers is made at Billingham showing on analysis percentages as below :—

	Nitrogen.	Phosphoric acid.		Potash.
		Water sol.	Insol.	
A . .	14·3	43·0	—	—
B . .	18·0	18·0	—	—
C . .	16·0	32·0	—	—
D . .	12·3	56·5	—	—
1 . .	12·5	12·5	—	15·0
2 . .	10·4	10·4	—	20·8
4 . .	10·4	20·8	—	10·4
5 . .	8·0	16·0	5·5	16·0
6 . .	7·5	26·0	6·0	7·5
7 . .	6·5	22·5	3·0	13·0

Gypsum.—This has in most cases but a small value for direct use as a manure. Where superphosphate is used, gypsum is an integral part of it. Gypsum is sometimes used as a drier to mix with damp or pasty fertilisers.

Borax is sometimes effectively used as a remedial application for " heart rot " in sugar beet, turnips and swedes and also for certain diseases of apples and of tobacco. It was conclusively proved by K. Warington as long ago as 1923 that traces of boron were essential to the development and flowering of broad beans, and it may well be that traces of boron in the soil are essential for most crops, in which case it appears probable that most soils contain a sufficiency of it. When used, applications are usually restricted to such small dressings as 15 to 20 lb. of borax per acre. If applied in dressings approaching the proportions of the dressings in which ordinary concentrated fertilisers are applied it may be disastrously poisonous.

Lime, Chalk and Marl.—These are mainly applied for the sake of the considerable amelioration of the soil which they effect, especially in the correction of " acidity." Burnt lime, fresh or slaked, is in common use. Freshly burnt lime is usually used in " lump " form, but can now also be obtained from cement factories in a finely ground state, in which condition much smaller dressings may be effectively used, though, of course, they need to be repeated from time to time. Finely ground chalk is now also obtainable from the same source; and there is a growing supply of finely divided calcium carbonate obtained as a by-product in the softening of calcareous water supplies.

Potassium Salts—(Those used as fertilisers are mainly the sulphate containing from about 48 to 53% K_2O and the chloride (commercially known as "muriate") containing KCl equivalent to about 50% K_2O. Lower grades of potassium chloride largely diluted with sodium chloride are also much in use. One grade containing the equivalent of about 12 to 14% K_2O is often sold under the misnomer "*Kainit*" —presumably because its potash equivalent is similar to that of the formerly popular natural mineral *kainite*, which if not yet exhausted is now rarely obtainable.

For most crops the sulphate or chloride may be used interchangeably, but for potatoes the sulphate is preferable. On freely draining soils the lower solubility of the sulphate may be advantageous, but on most soils, even with the chloride, there is little chance of loss by drainage, as the potassium is readily fixed by " base exchange " in the clay fraction of the soil.

The Relative Value of Manures.

Of the nitrogenous fertilisers nitrates are the most rapidly active form of nitrogen. Comparisons between sodium nitrate and ammonium salts, containing similar amounts of nitrogen, have been made for many years at Rothamsted, and also at Woburn. With cereal crops the nitrate, on an average, yields, nitrogen for nitrogen, distinctly more corn and considerably more straw than ammonium salts. On grassland, the relative superiority of nitrate as regards yield of hay, is about the same as with cereals. For potatoes, ammonium sulphate is usually preferred to nitrate. For mangel-wurzel, or sugar beet, the nitrate is superior. Nitrates and ammonium salts, in favourable circumstances, give most of their effect in the first year of their application.

The constant use of ammonium sulphate on soils poor in lime tends to cause a deleterious acid condition of the soil unless lime is occasionally applied. On such soils the use of sodium nitrate in alternate years has been suggested, since the residual effect of this salt in the soil is alkaline.

Cyanamide, under favourable conditions, gives results similar to those obtained from a corresponding quantity of ammonium sulphate, but its action depends upon its time of application and upon suitable weather and, probably, upon the texture and composition of the soil, as well as on biological considerations. It is best used after admixture with superphosphate, though it has the incidental effect of " precipitating " soluble phosphate. Unless supplied in the granulated form it is not a pleasant substance to handle in its raw condition, and, if sown alone, it should be sown by means of a mechanical distributor.

The effect of organic nitrogenous manures differs in different soils. In a clay soil, bones decompose so slowly as to be of little value. Organic manures, as shoddy, oilcake, bones and farmyard manure, yield only a portion of their nitrogen to the crop during the first year, and several years will elapse before the supply is exhausted. The continued use of such manures increases the proportion of nitrogen in the soil. The proportion of the nitrogen in the manure that is recovered in the crop is frequently smaller than that obtained under favourable circumstances in one season from the application of sodium nitrate or ammonium sulphate, the slowly acting manures being, in the case of arable land, subject to an annual loss of nitrogen as nitrates by drainage. Organic nitrogenous manures are more active in proportion as they are finely divided, and when applied to a well-aerated soil. They are best applied in autumn, while nitrates and ammonium salts should be applied in spring.

At the close of the section devoted to farmyard manure, (page 63) reference was made to the now recognised existence of " auximones " (plant growth-stimulants) in some forms of decaying organic matter having a function additional to the mere supply of actual plant food—with the suggestion that this may have some bearing on the well-known fact that for some purposes farmers show a preference for organic nitrogenous fertilisers over those of inorganic origin—such as nitrate or sulphate of ammonia.

The relative value of different forms of phosphates has been a subject of much controversy. Some mineral phosphates (as apatite) having been found almost useless as manure, it was too hastily concluded that (with the exception of bone and guano phosphates) only phosphates soluble in water were effective. It has, however, been maintained that very fine grinding will render any phosphate as available as soluble phosphate.

In considering the subject it should be borne in mind that the phosphates in the soil, on which plants feed, are not soluble in water, drainage waters being free from phosphoric acid. Soluble phosphate when applied to a fertile soil is quickly precipitated, and is generally finally converted into a hydrated ferric or aluminium phosphate. The practically insoluble phosphates of the soil are dissolved either by the acid sap of the root hairs immediately before absorption by a crop or (as is now considered more probable) by the carbonic-acid-laden water of the soil.

One great advantage possessed by a phosphate soluble in water consists in its diffusibility. When rain falls after an application of superphosphate or other water-soluble phosphate, the phosphoric acid is distributed in the soil more perfectly than can be achieved by any other mode of application, and consequently a greater number of root hairs may come in contact with it. Superphosphate is thus more immediately effective than other forms of phosphate. The superiority of superphosphate is, however, not shown in the case of some soils very poor in lime, in which any additional supply of acid matter is hurtful to the plant; in such cases an assimilable undissolved phosphate may produce a better result. On such soils (poor in lime), basic slag, guano or fine bone meal find an appropriate place.

Numerous experiments have been made regarding the assimilability of mineral phosphates when finely ground. It appears that apatites and other crystalline phosphates not disintegrated in the soil, have a very small manurial effect even when finely ground. The majority of non-apatitic mineral phosphates are, however, effective when very finely ground, but to a different extent on different soils. The conditions favourable to the use of undissolved phosphates are presence of humus and scarcity of lime. On the moor soils of Germany, where such conditions prevail, basic slag has had its greatest success. A calcareous soil is the one least suitable for the use of undissolved phosphates.

It is generally admitted that precipitated dicalcium phosphate is nearly equal in effect to soluble phosphate. Phosphates that are soluble in ammonium citrate (including the reverted phosphate of superphosphate) may be safely regarded as assimilable by plants; in America they are regarded as of about equal value with water-soluble phosphate; that they are so always is certainly open to doubt. But phosphates that are insoluble in ammonium citrate are often effective as manure. Ammonium citrate gives thus no safe distinction between assimilable and non-assimilable phosphates, though it affords a useful approximate means of determining "reverted" phosphate in superphosphate.

As a measure of ready availability in basic slag, a 2% solution of citric acid has now superseded ammonium citrate.

SPECIAL METHODS OF ANALYSIS.

The enormous quantity of fertilisers and of their components bought and sold upon the results of analysis has led to great attention being paid to the question of accurate and speedy analytical methods. To enter into a discussion of all the methods which have been suggested, or even of those which have been "officially" recognised by the associations of agricultural analysts or manufacturers in different countries, is here impossible.

In the analysis of fertilisers, the object is sometimes merely the determination of a definite fact, such as the percentage of total nitrogen or the percentage of total phosphoric acid. In such cases there are diverse methods available. Sometimes, however, the analysis is needed for such a purpose as the determinations of "soluble" phosphoric acid. Here much depends upon the interpretation of the word "soluble," since solubility depends not merely on the nature of the solvent, but upon its proportion to that of the material acted upon and the mode and duration of its application. It is therefore necessary to define "solubility" before determining it. Unfortunately, different interpretations of solubility have been in vogue in different countries, causing occasional confusion in international trade, but efforts to arrive at international agreement have been attended with some, though only a partial, measure of success.

ANALYSIS OF RAW MINERAL PHOSPHATES.

Determination of Phosphoric Acid.—The phosphoric acid in mineral phosphates may be accurately determined either by the use of molybdic acid or by what is sometimes called the citric-oxalic-magnesium method, without the intervention of molybdic acid.

There are several modifications of the molybdate method which give fairly accurate and therefore concordant results in the hands of careful workers. Their one common disadvantage is that the quantity of sample represented in the portion of solution finally worked upon is necessarily smaller than in the alternative procedure, and consequently any errors due to inaccuracy of calibration of flasks or pipettes or to lack of exactness in using them, are correspondingly multiplied; and the same observation obviously attaches to errors incidental to the washing of precipitates, the efficiency of filters and the operations of weighing. There is cogent reason for supposing that many disagreements sometimes attributed to the use of alternative methods are due to insufficient appreciation of some of these sources of error, or to the non-observance of the precautions necessary to avoid them. When, as is often the case, as little as 0·2 g. of raw phosphate is used in the determination, a single milligram of magnesium pyrophosphate (the form in which the phosphate is weighed) is equivalent to approximately 0·7% of tricalcium phosphate—a grave consideration in the case of large cargoes, the price of which is exactly adjusted to the results of analysis, even to the second place of decimals.

A reliable modification of the molybdate method as applied to the analysis of raw mineral phosphates which has been in use for many years is that of G. Jörgensen, who has devoted much time and attention to the matter.

Jörgensen's method was originally published in Denmark, but an account of it, communicated by himself, was published in the Analyst, 1909, **34**, 392, and it is now generally regarded as of standard accuracy. It is as follows :—

Method of Jörgensen—5 g. of the mineral phosphate are dissolved in 20 ml. of nitric acid in a 250 ml. flask. After gentle boiling for 15 minutes, the contents of the flask are cooled, made up to 250 ml., and filtered. To 50 ml. of the filtrate (=1 g. of the phosphate) in a beaker-flask, 165 ml. of the molybdic solution are added, and the flask and its contents placed in a water-bath at a temperature of 50° for 10 minutes, with occasional stirring. After cooling and standing, the supernatant liquid is poured through a filter and the precipitate is washed 10 times by decantation with the acid ammonium nitrate solution, about 20 ml. being used for each washing. The filtrate should be tested with more molybdic solution to see that the precipitation is complete. The washed precipitate is dissolved in 100 ml. of 2½% ammonia solution, and filtered, if necessary, through the filter which served for its separation, the filter being washed 8 times with ammonia solution, until the final volume is about 180 ml. The beaker-flask is covered with a clock-glass, the contents brought just to boiling-point, and 30–35 ml. of the magnesia mixture added drop by drop from a burette, the whole being well stirred and allowed to cool with frequent stirring as long as it remains warm. If the precipitate is not compact and crystalline, the stirring should be continued longer. After standing for at least 4 hours, the precipitate is filtered off, using a platinum (Gooch) crucible packed with spongy platinum (or, presumably, ignited asbestos) and washed with the 2½% ammonia solution until free from chlorides, and once with alcohol. It is then dried, heated (at first gently), and then ignited strongly, cooled and weighed as $Mg_2P_2O_7$.

The solutions used by Jörgensen are as follows :—

Molybdic Solution.—100 g. of ammonium molybdate are dissolved in 280 ml. of ammonia of sp.gr. 0·97, and 300 ml. of this solution poured with vigorous shaking into 700 ml. of nitric acid of sp.gr. 1·21, the mixture being allowed to stand for 24 hours.

Wash Fluid for Molybdic Precipitate.—40 g. of ammonium nitrate and 10 g. of nitric acid per litre. The author prepares this by mixing 90 ml. of nitric acid of sp.gr. 1·4 with about 1,500 ml. of water, adding 80 ml. of ammonia of sp.gr. 0·91 and making up to 2 litres.

Magnesia Mixture.—50 g. of pure crystallised magnesium chloride and 150 g. of pure ammonium chloride, dissolved and made up to 1 litre.

Wash Fluid for Ammonium-Magnesium Precipitate.—Ammonia solution containing 2½% NH_3. (This may be made by diluting 100 parts of ammonia of sp.gr. 0·91 with water to 1 litre.)

St. Gobain (Sanfourche) Method.—Comparatively recently, however, another form of the molybdate method has assumed importance owing to its having been adopted, as an alternative to Jörgensen's method, at a conference of superphosphate manufacturers at Hamburg in 1934, and as this process is now much in use on the Continent and is sometimes imposed as an obligatory condition in " arbitration " analyses, details must here be recorded.

1·5 g. of the finely ground mineral phosphate is treated with 20 ml. of nitric acid (sp.gr. 1·38) and the solution evaporated to dryness on a sand-bath at 115–120°C. The residue is taken up in 15 ml. of nitric acid, diluted with 200 ml. of water and boiled for 2 minutes, allowed to cool and diluted to a volume of 500 ml. The solution is filtered through a dry filter and 50 ml. (=0·15 g. of the phosphate) are placed in a 500 ml. Erlenmeyer flask and diluted with water to a volume of 100 ml. 30 ml. of nitric acid are added, followed by 20 ml. of ammonia (sp.gr. 0·924) and brought to a boil. The flask is removed from the flame and immediately there is added, drop by drop, from a pipette or stoppered funnel, 15 ml. of a solution of pure ammonium molybdate (150 g. per litre), avoiding dropping this down the sides of the flask. At the same time the flask is continuously rotated so as to obtain a precipitate free from occluded molybdic acid. The whole is then shaken for 1 minute and allowed to stand for 20 minutes, after which there are two alternative modes of procedure—gravimetric or volumetric.

Gravimetric Method.—The liquid is decanted through a tared Gooch crucible and the precipitate washed 4 times by decantation with a wash solution having a temperature of 70–80°C. and consisting of a mixture of 865 ml. distilled water, 85 ml. nitric acid and 50 ml. of ammonia (sp.gr. 0·924). The whole of the precipitate is transferred to the crucible, removing any portions adherent to the sides with a rubber-tipped glass rod. The filter is washed 4 or 5 times with the wash solution, until the filtrate gives no colour with potassium ferrocyanide. The precipitate is drained completely by the pump, dried in an oven, covered and placed in an electric muffle, the temperature of which is raised gradually to 500–550°C., which temperature is maintained for an hour, when the precipitate should be of a uniform blue-black colour. After complete cooling in a desiccator it is weighed. The weight of precipitate multiplied by $0{\cdot}03946 = P_2O_5$.

Volumetric Method.—The phospho-molybdic precipitate obtained as hereinbefore described is washed by decantation twice (cold) with the wash solution already mentioned, the decanted liquid being passed though a filter of hardened paper of a diameter of 125 mm., on to which, by aid of the same solution, the precipitate is finally collected. After complete draining the precipitate is washed twice on the filter with distilled water which has been used to rinse the flask, and then further 6 times with distilled water, taking care to drain completely after each washing. The final washing must be free from acidity to the extent that after the addition of a drop of phenolphthalein it should be reddened by the addition of a single drop of $N/10$ $NaOH$.

The filter and precipitate are then replaced in the flask with the addition of 50 ml. of $N/2$ sodium hydroxide solution, the whole being well stirred and the filter squeezed out against the sides of the flask by means of a glass rod, where it is momentarily allowed to remain. There are then added 12·5 ml. of a previously neutralised 40% formaldehyde solution containing 0·015 g. of phenolphthalein per 100 ml. (or 17·5 ml. if the sample contains more than 70% phosphate). The filter paper is re-plunged in the liquid, well stirred and again brought to the side of the flask and pressed out. *N*/2 hydrochloric acid solution is added until the red phenolphthalein colour disappears, when the filter paper is again immersed, stirred, brought to the side and pressed out, the addition of acid being continued until the colour again disappears. When the filter is again immersed there should be no return of the red colour, otherwise the addition of acid is continued as before. At complete neutralisation, if V is the volume of hydrochloric acid added (50 ml. – V ml.) × 0·001362 = weight of P_2O_5.

Either modification of this St. Gobain (Sanfourche) process has been found in the hands of the present writer to give results closely agreeing with those obtained by Jörgensen's method, provided that the analysis process is carried out with meticulous care. But it must be remembered that, as the weight of sample in the portion of solution operated on is only 0·15 g., any experimental error is necessarily multiplied 6½ times more than is any error incidental to Jörgensen's method in which the quantity of phosphate operated upon is 1 g.

Citric-Oxalic-Magnesium Method.—The phosphoric acid (and incidentally the calcium) may be correctly determined in the following way. 2 g. of the mineral phosphate are treated with 25 ml. of strong hydrochloric acid in a beaker covered with a clock-glass to avoid loss by spraying. After a few minutes' warming, the clock-glass is washed back into the beaker and removed, the beaker being placed in a water-bath and the contents evaporated to dryness. This results in the elimination from solution of not only silica, but of fluorine compounds, the removal of which is essential to the accuracy of the process. Mere evaporation to dryness with a small quantity of hydrochloric acid is insufficient to ensure this removal. It is necessary to use at least the large quantity of acid specified (25 ml.), so that its evaporation may extend over several hours. (The non-observance of this precaution is a fruitful source of error, resulting in the subsequent formation of magnesium fluosilicate and consequent over-estimation of phosphoric acid). The dry residue is taken up with 5 or 10 ml. of hydrochloric acid and about 20 ml. of water, and warmed. The silica, together with pyrites or other insoluble matters, is filtered off and thoroughly washed. To the filtrate and washings (measuring about 150 ml.), 4 g. of powdered citric acid are added and 3–4 g. of powdered ammonium oxalate. The solution is heated nearly to boiling, and rendered just alkaline with dilute ammonia (sp.gr. about 0·970) and excess of acetic acid is immediately added and the liquid is boiled for a few moments. The calcium oxalate is immediately filtered off and washed several times with boiling water, dried, and ignited over a yellow Argand flame, and weighed as $CaCO_3$. The precipitate contains all the calcium. It may contain very minute quantities of ferric oxide, aluminium oxide or manganese oxide, and a minute quantity of phosphoric acid. On this account the precipitate, after being weighed, is dissolved in dilute hydrochloric acid, the solution being boiled and treated with a slight excess of recently diluted ammonia. The small precipitate which forms is filtered through a small filter, washed and redissolved in a little dilute acid, the solution being boiled and again treated with a slight excess of ammonia. The precipitate is washed, ignited and weighed. If this small precipitate weighs only 5 or 6 milligrams or less (as is usually the case in the hands of a practised worker), it may be assumed that the precipitate contains P_2O_5 equivalent to half its own weight of $Mg_2P_2O_7$, this assumption being based on the analysis of a large number of such precipitates. But if, owing to unskilful work or to any peculiarity in the mineral under investigation, the quantity is greater, the little precipitate may be redissolved in hydrochloric acid, with the addition of about 0·1 g. of citric acid, and its solution added to the original filtrate from the calcium oxalate precipitate.

This filtrate is made strongly ammoniacal and the phosphoric acid precipitated by the gradual addition of magnesium mixture, a large excess being finally added. The gradual addition and vigorous stirring are both necessary to ensure that the precipitate comes down in a compact crystalline form. The whole bulk at this stage will be about 350 ml. After 2–3 hours, during which the liquid is frequently stirred—or after standing, if more convenient, overnight—the greater part of the liquid is decanted off through a close filter, leaving about 40 ml. of it in the beaker with the precipitate. The filter is washed with dilute hydrochloric acid, the washings being used to redissolve the precipitate in the beaker. After complete re-solution, the contents of the beaker are rendered ammoniacal by slowly dropping in dilute ammonia with vigorous stirring until the precipitate assumes as before a dense crystalline form. Excess of ammonia solution (sp.gr. 0·880), equal to about one-fifth or one-sixth of the bulk of the liquid, is added and the whole allowed to stand with occasional vigorous stirring for at least 1 hour. The precipitate is then filtered, washed well with ammonia (sp.gr. 0·970), dried, ignited and weighed as $Mg_2P_2O_7$.

The re-solution and second precipitation of the ammonium magnesium phosphate is an essential feature of the process, since in the first precipitation small quantities of magnesium oxalate are usually formed. The non-observance of this precaution has been a frequent source of " high " results.

The presence of ammonium citrate and ammonium oxalate results in the retention in solution of a minute quantity of P_2O_5. In earlier days it was usual to precipitate the ammonium magnesium phosphate, in a flocculent form, by the sudden addition of ammonia and magnesium mixture, and under these circumstances (*see*, for example, the original directions of Fresenius) a very substantial correction was necessary for solubility of the precipitate. Crystalline precipitation, however, reduces this to a minimum, and the accurate determination by molybdic acid of the phosphoric acid in the evaporated and ignited filtrates obtained in a large number of analyses of numerous grades and varieties of phosphate indicates that, if the process be carried out as here described, the quantity of P_2O_5 which escapes precipitation corresponds to an average of approximately 0·0025 g. of $Mg_2P_2O_7$, which quantity must be added to the weight of $Mg_2P_2O_7$ obtained, together with half the weight of the small ammonia precipitate (obtained from the calcium oxalate precipitate), unless this was redissolved into the main filtrate (*see above*).

If the precautions herein set forth are observed, the results will be identical with those obtainable by the accurate working of the molybdate method (Jörgensen).

Direct Magnesium Precipitation without Removal of Calcium.—This method consists in adding to the acid solution of the phosphate a large excess of citric acid, sufficient to prevent calcium precipitation, and of ammonia, and in the direct precipitation of the phosphoric acid by magnesium mixture, without re-solution. This method (with certain precautions) answers well for basic slag (*see* later), and in some hands appears to give good results with mineral phosphates. It does not, however, answer equally well for all phosphates, and the result, even when accurate, owes its success to a balance of positive and negative errors, since the precipitate finally weighed does not consist of pure $Mg_2P_2O_7$, as is assumed to be the case. For rough work, as in phosphate prospecting, when an error of 0·5% or so is of small moment, it is excellent, being expeditious and involving a minimum of trouble. It is essential that silica should be eliminated by preliminary evaporation of the acid solution to dryness as in the preceding section.

Determination of Ferric Oxide and Alumina in Mineral Phosphates.

The solvent used should be hydrochloric acid rather than *aqua regia*. The latter is sometimes recommended. For many phosphates it is perhaps immaterial which solvent is used. But some phosphates (such as American river pebble phosphates) contain much pyrites. If *aqua regia* is used, this is dissolved and included as ferric oxide—which is misleading, seeing that pyrites is not attacked by the sulphuric acid used in superphosphate making, and is consequently non-injurious. It should, therefore, be eliminated with the silica, as is the case if hydrochloric acid be used as the solvent.

There are two methods in use which accurately determine ferric oxide and alumina.

Acetate Method.—2 g. of phosphate are treated with strong hydrochloric acid. The solution is evaporated to dryness and the residue redissolved in acid and water and filtered from the silicious residue. The filtrate is oxidised by addition of bromine water until orange-coloured, nearly neutralised with ammonia, cooled and precipitated still cold with a liberal excess of ammonium acetate solution containing an excess of acetic acid. After standing some hours, the precipitate is filtered off and washed with hot water.

The bulky precipitate contains all the ferric oxide and alumina (as phosphates), together with a varying quantity of calcium phosphate. It is dried, ignited and weighed. It is then dissolved in a very small quantity of hydrochloric acid and about 1 g. of citric acid and 0·5 g. of ammonium oxalate added, slight excess of ammonia, and then excess of acetic acid. After simmering gently for ½ hour the calcium oxalate is filtered off, ignited and weighed as carbonate. The phosphoric acid is then determined, exactly as in the citric-oxalic-magnesium method of phosphate analysis already described—except that the operation is conducted all through in solutions of very small bulk. The sum of the lime and phosphoric acid deducted from the weight of the ammonium acetate precipitate will give the ferric oxide and alumina. The iron is determined by precipitating with ammonium sulphide the total filtrates and washings from the precipitation and reprecipitation of the ammonium magnesium phosphate. If allowed to stand for an hour or two at a temperature of about 80°C., the precipitate settles well, and may be rapidly filtered, washed with hot water to which a little ammonia and ammonium sulphide are added, ignited strongly and weighed as Fe_2O_3. The alumina is obtained by difference. The method is tedious, but accurate.

Modified Glaser Method.—The following method, modified from that of Glaser (which originally, but incorrectly, assumed a constancy of composition of the precipitate of mixed phosphates) is somewhat shorter, and gives results identical with those obtained by the method just described.

4 g. of the phosphate are treated with about 25 ml. of strong hydrochloric acid and evaporated to dryness. The residue is taken up with 10 ml. of strong sulphuric acid, about an equal bulk of water being cautiously added. After digestion in a water-bath for about ½ hour, the cake of calcium sulphate is well broken up by stirring with a glass rod, and the whole contents of the beaker are washed into a 200 ml. flask with ordinary strong alcohol (methylated spirit), and allowed to remain for an hour with frequent shaking. The contents are then made up (with spirit) to 200 ml., again well shaken and filtered rapidly. Of the clear filtrate, 100 ml. (=2 g. of the sample) are evaporated in a glass or porcelain basin until the residue fumes and begins to "char," when it is washed with a little hot water into a beaker and mixed with sufficient bromine water to make it strongly orange-coloured. After standing for ½ hour, the liquid is heated nearly to boiling and precipitated with slight excess of ammonia, kept in a water-bath for ½ hour, and made slightly acid with acetic acid. The precipitate (which, under these conditions, contains only phosphoric acid, ferric oxide and alumina) is filtered off, washed with a slightly ammoniacal 20% solution of ammonium nitrate, dried, ignited and weighed. It is then dissolved in a little hydrochloric acid, 1 g. of citric acid is added to the solution, which is then made ammoniacal, and the phosphoric acid determined by precipitation with magnesium mixture. The total bulk of fluid should be kept within about 100 ml. In this case, the

precipitate of ammonium magnesium phosphate does not need re-solution and re-precipitation, no oxalate being present. The iron is precipitated from the filtrate with ammonium sulphide, as in the preceding process, and the alumina is arrived at by difference.

Lasne Process for Direct Determination of Alumina.—Objection has been sometimes raised to the fact that, while in the processes already described, ferric oxide is determined directly, alumina, on the other hand, is taken by difference. The following process, as described by H. Lasne, affords a correct method for the direct determination of alumina. It has been frequently tested by the writer of this article, in whose experience it gives results substantially identical with those obtained by the two differential methods already quoted. In either case, whether a direct or an indirect method be used, success depends upon delicacy of manipulation and strict attention to the details prescribed.

5 g. of phosphate are treated with hydrochloric acid, the solution being evaporated to dryness, taken up with 60 ml. of 10% hydrochloric acid, and digested at about 100°C. for 1 hour. The solution is diluted to 500 ml. and filtered, 125 ml. being taken for the determination of alumina. 5 g. of caustic soda (free from silica and alumina) and 1 g. of sodium phosphate are dissolved in 20 ml. of distilled water in a nickel basin. Into this solution the 125 ml. of phosphate solution are poured, with constant stirring, and kept for about an hour at a temperature of about 100°C., with occasional stirring, preferably with a nickel spatula. The liquid is cooled, and made up to 250 ml. in a glass flask. The contents are filtered, and 200 ml. of the filtrate (=1 g. of the phosphate sample) mixed with 30 ml. of a solution of ammonium chloride (125 g. per litre), sufficient hydrochloric acid being added to dissolve such precipitate as is formed. Ammonia is then added in very slight excess. After boiling for 5 minutes, the precipitate is filtered off, washed slightly once with water and redissolved through the filter into the original beaker with a little 10% hydrochloric acid, the filter being washed with water 5 or 6 times. The solution is treated with 3½ ml. of a solution of pure ammonium phosphate (10 g. per 100 ml.), and ammonia added till a permanent precipitate is formed, and then sufficient dilute hydrochloric acid to dissolve again the precipitate. The fluid is diluted to 250 ml., when 10 ml. of a solution of ammonium thiosulphate (15 g. per 100 ml.) are poured in. After ½ hour's boiling, 5 drops of a saturated solution of sodium acetate are added, and, after 5 minutes' further boiling, the precipitate is filtered off and washed 7 or 8 times with water. The precipitate, which is granular and not gelatinous, is ignited to constancy, and assumed to have the composition of pure aluminium phosphate. Its weight multiplied by 0·418 gives the alumina in 1 g. of the sample.

ANALYSIS OF SUPERPHOSPHATE, DISSOLVED BONES, ETC.

"Moisture" is conventionally determined by simply drying to constancy at 100°C. The result should, in such cases, be stated as "moisture (*i.e.* loss at 100°C.)" because the figure obtained is not moisture in the true sense, since it includes a varying quantity of water of hydration. True moisture can only be determined by drying to constancy *in vacuo* over sulphuric acid. The result in that case should be stated as "true moisture (*i.e.* loss *in vacuo*)."

Determination of Soluble Phosphate.—Formerly in England (and still in America), solubility was determined by fractional exhaustion with successive small quantities of cold water (with or without a final exhaustion with hot water). On the Continent of Europe it has long been usual to dissolve in a large bulk of water at one operation. The former method usually extracted somewhat more phosphoric acid than the latter, since some interaction occurs on dilution between the dissolved phosphoric acid and the "insoluble" phosphate. As this depends upon the chemical composition of the original phosphate, and also on the degree of dilution, the differences in the results obtained by the two methods of extraction are variable—being sometimes negligible, but occasionally serious.

The following method of extraction of soluble phosphate, adopted at a meeting of the International Congress of Applied Chemistry, is now usually adopted in England, and is the method officially laid down by the Ministry of Agriculture (1932) for use under the Fertilisers and Feeding Stuffs Act, 1926:

In the case of superphosphates, dissolved bones and similar substances, "20 g. of the sample shall be continuously agitated for 30 minutes in a litre flask with 800 ml. of water at room temperature. The flask shall then be filled to the mark, and again shaken, and the contents shall be filtered."

The phosphoric acid is then determined in an aliquot part (50 ml.) of the solution which is first boiled with 20 ml. of concentrated nitric acid to ensure that all the dissolved phosphoric acid is in the ortho form.

The determination of phosphoric acid is directed to be made either by the molybdate process, prescribed in a form that is essentially that of Jörgensen, already described; or, alternatively, by direct precipitation without the intervention of molybdic acid.

In the latter case, the 50 ml. of water solution after boiling, as aforesaid with nitric acid, are neutralised with ammonia and mixed with 50 ml. of ammonium citrate solution (110 g. of citric acid and 400 ml. of ammonia of sp.gr. 0·9135 made up to 1 litre) and raised to boiling point. Magnesia mixture is then added drop by drop with constant stirring and after cooling the precipitate is allowed to stand with occasional stirring for at least 4 hours, then filtered, washed with 2% ammonia, dried, ignited and weighed as $Mg_2P_2O_7$.

DETERMINATION OF TOTAL PHOSPHATE IN FERTILISERS.

This may, in most cases, be carried out by the methods already described for the analysis of raw mineral phosphates, materials containing much organic matter being first incinerated.

The official method prescribed (1932) in England under the Fertilisers and Feeding Stuffs Act, however, which should be adhered to in disputed cases, is the molybdate method.

The official prescription of the Ministry of Agriculture (1932) for determination of total phosphate in fertilisers is as follows :—

" (A) A weight portion of the sample shall be heated with concentrated sulphuric acid until all organic matter is destroyed and the phosphoric acid is completely in solution. After dilution the solution shall be filtered, the insoluble matter throughly washed and the filtrate made up to a definite bulk. The phosphoric acid shall be determined by the method described in paragraph (iv) (*e*) in an aliquot part of the solution which shall first be nearly neutralised and then acidified with nitric acid. The insoluble matter is to be washed from the filter, re-extracted with acid and any phosphoric acid present in the solution is added to the main quantity.

" (B) *Alternative Method.*—A weighed portion of the sample shall be incinerated or otherwise treated to destroy organic matter, if present. When direct incineration is employed, the weighed portion of the sample shall be treated, before being heated, with a nitrate or other oxidising material to prevent loss of phosphoric acid during heating or subsequent treatment. The residue (or the weighed portion taken, if no organic matter is present) shall be dissolved in hydrochloric acid, with the addition, if necessary, of nitric acid, and the solution shall be evaporated to dryness or, if much calcium is present, to a syrupy consistency to fix silica. The residue shall be boiled with nitric acid and, when much iron is present, with hydrochloric acid also. After dilution the solution shall be filtered, the insoluble matter thoroughly washed and the filtrate made up to a definite bulk. The phosphoric acid shall be determined in an aliquot part of the solution by the method prescribed in paragraph (iv) (*e*). The insoluble matter is to be washed from the filter, re-extracted with acid and any phosphoric acid present in the solution added to the main quantity.

" *Molybdate Method.*—(iv) (*e*) To the solution, which should contain not more than 0·4 g. of phosphoric acid (P_2O_5), and preferably from 0·1 to 0·3 g., (obtained by any of the methods described in preceding paragraphs) 100–150 ml. of molybdic acid solution prepared as described below, or an excess of such solution, *i.e.*, more than is sufficient to precipitate all the phosphoric acid present in the solution, shall be added and the vessel containing the solution shall be placed in a water bath maintained at 70°C. for 15 minutes or until the solution has reached 70°C. It shall then be taken out of the bath and allowed to cool and the solution shall be filtered, the phospho-molybdate precipitate being washed several times by decantation and finally on the paper with 1% nitric acid solution. The filtrate and washings shall be mixed with more molybdic acid solution and allowed to stand for some hours in a warm place in order to ascertain that the whole of the phosphoric acid has been precipitated. The phospho-molybdate precipitate shall be dissolved in cold 2% ammonia solution, prepared as described below, and about 100 ml. of the ammonia solution shall be used for the solution and washings. The solution shall be raised to the boiling-point, the beaker removed from the burner and 15–20 ml. of magnesia mixture, prepared as described below, or an excess of such mixture, *i.e.* more than sufficient to precipitate all the phosphoric acid present, shall then be added drop by drop, with constant stirring. The stirring shall be continued at intervals so long as the liquid remains very warm. After standing at least 4 hours with occasional stirring, the precipitate shall be filtered off, washed with 2% ammonia solution until free from chloride, dried and finally weighed as magnesium pyrophosphate. The filtrate and washings should not exceed 200 ml., and are to be tested by the addition of more magnesia mixture."

Molybdic Solution.—" The molybdic acid solution shall be prepared as follows :—

> " 125 g. of molybdic acid and 100 ml. of water shall be placed in a litre flask and the molybdic acid shall be dissolved by the addition, while the flask is shaken, of 300 ml. of 8% ammonia solution, prepared as described below. 400 g. of ammonium nitrate shall be added, the solution shall be made up to the mark with water and the whole added to 1 litre of nitric acid (sp.gr. 1·19). The solution shall be maintained at about 35°C. for 24 hours and then filtered."

Magnesia Mixture.—" The magnesia mixture shall be prepared as follows :—

> " 110 g. of crystallised magnesium chloride and 140 g. of ammonium chloride shall be dissolved in 1,300 ml. of water. This solution shall be mixed with 700 ml. of 8% ammonia solution and the whole shall be allowed to stand for not less than 3 days and shall then be filtered."

Ammonia Solutions.—" The 8% ammonia solution shall be prepared as follows :—

> " One volume of ammonia solution of sp.gr. 0·880 shall be mixed with three volumes of water. This solution shall then be adjusted by the addition thereto of more strong ammonia solution or water as required until the specific gravity of the solution is 0·967.

" The 2% ammonia solution shall be prepared as follows :—

> " One volume of 8 per cent. ammonia solution shall be mixed with three volumes of water."

Reverted Phosphate.—The " reverted " phosphate in superphosphate may be estimated as follows : 2 g. of the sample are stirred up in a beaker with successive quantities of 50 ml. of water, each portion, after settling, being decanted off through a filter. The water-soluble phosphate having been thus approximately removed, the matter on the filter is washed back into the beaker with a little water, and the undissolved matter is digested overnight at room temperature with 100 ml. of a strong solution of ammonium citrate containing excess of ammonia, then warmed to 40°C. for an hour, with frequent shaking, and the insoluble matter filtered off and ignited and the phosphoric acid in it determined. The difference between this and the water-insoluble phosphoric acid is taken as " reverted " phosphoric acid.

Citrate-Soluble Phosphoric Acid.—Apart from the mere question of " reverted " phosphate, many fertilisers are dealt in, on the Continent and in America, on the basis of " citrate-soluble " phosphoric acid. On the Continent the citrate solution in common use for ascertaining " citrate solubility " is the alkaline ammonium citrate known as " Petermann " solution. This is made by dissolving 173 g. of citric acid in water and adding 537 ml. of ammonia solution of sp.gr. 0·960 and diluting to 1 litre.

The method is frequently applied to precipitated bone phosphates, when 1 g. of the sample is triturated in a mortar several times with successive quantities of Petermann solution, the decantations being collected in a 500 ml. flask into which the undissolved matter is finally washed with further quantities of the citrate solution until 200 ml. of solution in all have been used. The flask and its contents are then allowed to stand overnight, heated in a water-bath at 40° for 1 hour, cooled, made up to 500 ml. with water, well shaken and filtered. An aliquot part of the solution is then boiled with nitric acid and the phosphoric acid determined by the molybdate method.

In America " citrate-soluble " phosphate is commonly regarded as " available " phosphate, as distinguished from total phosphate, in certain types of fertiliser.

The solution used in America, however, is a neutral solution of ammonium citrate—in contrast to the Petermann solution which, as already indicated, is alkaline.

The American neutral solution has a sp.gr. of 1·09 at 20°C. and a p_H of 7·0. It is made by dissolving 370 g. of crystallised citric acid in 1,500 ml. of water and nearly neutralising by the addition of 345 ml. of ammonia solution containing 28–29% of ammonia. A small measured portion (10 ml.) of the resultant solution is then adjusted to a p_H of 7·0 using phenol-red as an indicator and noting the quantity of a weak ammonia solution necessary to effect this adjustment. A corresponding quantity of ammonia is thus added to the bulk of the solution which is then made up to 2 litres.

The American estimation of " available " phosphate in the case of acidulated fertilisers is to place 1 g. on a filter paper and wash with successive quantities of water until the filtrate measures 250 ml. The water-soluble phosphoric acid is determined in this by the molybdate method. The water-insoluble matter (including the paper filter) is plunged into a 250 ml. flask containing 100 ml. of the neutral citrate solution previously raised to a temperature of 65°C. The flask is closed with a rubber stopper and shaken until the paper is disintegrated. The flask and contents are kept for an hour at 65°C. with frequent shaking, filtered as rapidly as possible and the undissolved matter washed with water at 65°C. until the filtrate and washings measure 350 ml. The insoluble matter is dried and ignited and the phosphoric acid therein determined by molybdate method.

The difference between this and the total phosphoric acid in the fertiliser is taken as " available "—being obviously resolvable by calculation into its water-soluble and water-insoluble components.

For non-acid fertilisers (except basic slag which is otherwise dealt with) the preliminary washing out with water is omitted, the operation being in other respects similarly conducted.

ANALYSIS OF BASIC SLAG.

In the analysis of basic slag, it is usual to determine (*a*) the percentage of " fine meal," (*b*) the percentage of total phosphoric acid, and (*c*) the percentage of phosphoric acid soluble in a 2% solution of citric acid.

Fine Meal.—Basic slag has always been sold here and abroad on a guarantee of fineness of grinding as gauged by the percentage passing through a standard sieve. The standard sieve almost universally in use since basic slag was first put on the market is a sieve made of the standard gauze known as " Amandus Kahl 100 E. Hamburg." In the regulations of the Ministry first issued under the Act of 1926, it was prescribed that the sieve to be used for ascertaining the fineness of grinding of basic slag (and also for ground limestone and ground raw phosphate or phosphate rock) should be made of wire of standard diameter of 0·141 mm., which should also be the length or width of each aperture, no wire being anywhere less than 0·137 mm. in diameter and no aperture greater than 0·155 mm. This was the 90-mesh sieve of the Institute of Mining and Metallurgy (I.M.M.), the dimensions being practically identical with those of the Amandus Kahl gauze 100 E. Later, however, this regulation has been amended by the prescription of the sieve known as the " British Standard Sieve, mesh No. 100." This sieve—which it should be pointed out differs from the 100 I.M.M. sieve—has been adopted as having meshes of substantially the same aperture as the previously prescribed sieve 90 I.M.M. or the Amandus Kahl sieve 100 E.

In well-ground slag from 80–90% should pass through the sieve. This is called the percentage of " Fine meal."

The *total phosphoric acid* may be determined as in mineral phosphates or as in other fertilisers.

An excellent method for slag, however, giving (by an admitted balance of errors) results identical with those of the molybdic method, is as follows: Treat 2 g. of the slag with strong hydrochloric acid and evaporate to dryness. Take up with 15 ml. of hydrochloric acid and 25 ml. of water, adding 20 g. of powdered citric acid. The silica is filtered off and washed, and the filtrate and washings (measuring about 170 ml.) are cooled, a large excess of magnesium mixture is added and about 50 ml. of strong ammonia. The liquid is stirred continuously for 15 or 20 minutes by aid of a mechanical stirrer, and allowed to stand with occasional stirring for 2 hours. The precipitate is filtered off, dried, ignited and weighed as $Mg_2P_2O_7$.

N.B.—This method is largely in use on the Continent, without observance, however, of the initial precaution of evaporating the acid solution to dryness to remove soluble silica. If the slag be merely digested with acid and the liquid filtered and precipitated without having been evaporated to dryness, the results may be seriously in excess of the truth. This has been pointed out by several investigators, but even now does not seem to be well recognised.

The phosphate soluble in 2% solution of citric acid is determined according to the method prescribed in the official directions of the Ministry of Agriculture, which is the method originally suggested by P. Wagner and generally known by his name.

" *Citric Soluble Phosphoric Acid (that is, Phosphone Acid Soluble in the Prescribed 2% Citric Acid Solution).*—5 g. of the sample shall be transferred to a stoppered bottle of about 1 litre capacity. 10 g. of pure crystallised citric acid shall be dissolved in water, the volume shall be made up to 500 ml., and the solution shall be added to the weighed portion of the sample in the bottle. To lessen the possibility of caking, the portion of the sample in the bottle may be moistened with 5 ml. of alcohol or methylated spirit before the citric acid solution is added; and in that case the volume of the citric acid solution shall be 495 ml. instead of 500 ml. The bottle shall be at once fitted into a mechanical shaking apparatus, and shall be continuously agitated during 30 minutes. The solution shall then be filtered through a large 'folded' filter, the whole of the liquid being poured on the paper at once. If not clear, the filtrate shall be again poured through the same paper.

" 50 ml. of the filtrate shall be taken and the phosphoric acid shall be determined by the molybdate method prescribed."

It may be added that 100 ml. of the solution (=1 g. of sample) can be used equally well for the molybdate determination.

The temperature at which the agitation with citric acid solution should be carried out is not mentioned in the current regulation of the Ministry of Agriculture, but is prescribed in Germany and also in America as 17·5°C. In the experience of the present writer it is desirable that the temperature of the solution and of the surrounding air should not be less than this.

The phosphate in the citric acid solution of the slag is frequently estimated by direct precipitation with magnesium mixture after adding a large excess of ammonium citrate. The results, however, are inaccurate (being too high) unless the citric acid solution of the slag is first evaporated to dryness with hydrochloric acid to eliminate soluble silica. If this precaution be taken, the results compare well with those of the molybdate method—which, on the whole, is quicker, and therefore preferable.

ANALYSIS OF POTASH SALTS.

Some commercial potash salts are of complex constitution, others are approximately simple salts. The methods of determining such constituents as calcium, magnesium, chlorine, etc., do not differ from those ordinarily employed in inorganic analysis, but the essential determination, namely, that of potash, may be described. Broadly speaking, two methods are in use, namely, the platinum chloride method and the perchloric acid method. The perchloric acid method was formerly but little used in this country, but owing to the great increase in the cost of platinum chloride has now come into wide use, and, while ranking with the platinum-chloride method as "official" in England, it has in practice largely superseded it.

The following are the details of the methods for determining potash in potash salts and in fertilisers officially prescribed in England.

Salts of Potash Free from Sulphates.

A weighed portion of the sample equivalent in potash content to 1·5–2·0 g. of potash (K_2O) is dissolved in water, filtered if necessary and made up to 500 ml.

Perchlorate Method.—50 ml. of the solution are placed in a small glass or porcelain basin and mixed with about 7 ml. of a 20% solution of perchloric acid (sp.gr. 1·125) free from chloric acid and evaporated on a hot plate or sand-bath until white fumes are copiously evolved. The precipitate is redissolved in hot water, a few drops of perchloric acid solution added and the whole again concentrated to the fuming stage. After cooling the residue is thoroughly stirred with 20 ml. of alcohol of sp.gr. 0·806–0·812 (95–96% of alcohol by volume). The precipitate is allowed to settle and the clear liquid poured through a weighed or counterpoised filter paper (or through a Gooch crucible), the precipitate being drained as completely as possible. The precipitate is washed by decantation with alcohol previously saturated with potassium perchlorate at the temperature at which it is used, the washings being poured through the paper (or Gooch crucible) on which the precipitate is finally collected, dried at 100°C. and weighed. The precipitate consists of $KClO_4$ and is calculated to its equivalent K_2O.

Platinum-Chloride Method.—50 ml. of the solution are acidified with hydrochloric acid and 10 ml. (or an excess) added of solution of platinum chloride containing 10 g. of platinum per 100 ml. After evaporation to a syrupy consistency in a water-bath, the contents of the basin are allowed to cool and washed by decantation with alcohol of sp.gr. 0·864 until the washings are colourless. The washings are passed through a weighed or counterpoised filter paper on which the precipitate is finally collected, washed with alcohol, dried at 100°C. and weighed as K_2PtCl_6 and calculated to the equivalent K_2O.

Salts of Potash Containing Sulphates.

A weighed portion of the sample equivalent to 1·5–2·0 g. of potash (K_2O) is boiled with 300 ml. of water to which has been added 20 ml. of hydrochloric acid. Barium chloride is continuously added, drop by drop, to the boiling solution until the sulphuric acid is completely precipitated. The liquid is cooled, made up to 500 ml. and filtered. 50 ml. of the filtrate are then evaporated to dryness, moistened with hydrochloric acid, again evaporated to dryness, taken up with dilute hydrochloric acid, filtered if necessary, and the potash determined by the perchlorate method or by the platinum-chloride method as already described.

Cobaltinitrite Method.—Alternatively, a weighed portion of the sample containing 1·5–2·0 g. of potash (K_2O) is boiled with 300 ml. of water made up to 500 ml. and filtered, and to 50 ml. of the solution are added 30 ml. of a solution of cobaltinitrite (made by dissolving 50 g. of cobalt nitrate and 300 g. of sodium nitrite in water, acidifying with 25 ml. of glacial acetic acid and diluting to 1 litre—the solution being filtered after standing 24 hours and kept in the dark). The mixture is stirred, allowed to stand for not less than 2 hours, filtered and the precipitate, consisting of potassium cobaltinitrite, washed with water containing a little cobaltinitrite solution. The precipitate is dissolved in hot dilute hydrochloric acid, evaporated to dryness in a small porcelain dish, redissolving in water, and the potash determined in the solution with perchloric acid as already described.

Potash in Guanos and in Mixed Fertilisers.

The directions in the Regulations of the Ministry of Agriculture (1932) directed that 10 g. of the sample shall be gently incinerated to char organic matter if present, and then heated for 10 minutes with 10 ml. of concentrated hydrochloric acid and boiled with 300 ml. of water and filtered. The liquid is raised to boiling point and powdered barium hydroxide is added until the liquid is slightly alkaline. It is then cooled, made up to 500 ml. and filtered. Of the filtrate 250 ml. are treated with ammonia and excess of ammonium carbonate and (while boiling) with a little powdered ammonium oxalate, cooled, made up to 500 ml. and filtered. (This method of precipitation with barium hydroxide has been found to involve some loss of potash—*see later*).

Of the filtrate 100 ml. are evaporated to dryness, and the residue heated gently over a low flame until all ammonium salts are expelled, the temperature being kept below that of low redness. The residue is moistened with concentrated hydrochloric acid, evaporated to dryness, taken up with dilute hydrochloric acid and filtered. The potash is then determined by the perchlorate method as already discribed.

As an alternative (official) method the liquid obtained by boiling the gently incinerated ash from 10 g. of the sample with 10 ml. conc. hydrochloric acid and finally with 300 ml. water is filtered into a ½ litre flask and the residue washed. The liquid is made up to 500 ml. and 50 ml. are taken, boiled with a solution of sodium nitrite to expel any ammonium salts, and evaporated to dryness. The residue is redissolved in water containing a little hydrochloric acid and sufficient sodium citrate added to prevent precipitation of phosphates. 30 ml. of cobaltinitrite solution are added and the same procedure is adopted as in the already described cobaltinitrite method for potash salts containing sulphates.

This alternative method gives correct results. But the other method involving the use of barium hydroxide to remove phosphoric acid as well as sulphates, unfortunately involves a source of error that has been long overlooked although this method of procedure has for many years been regarded as an accepted matter of routine, and the method will probably be amended when revised regulations are issued. When the potash content is large there is an appreciable loss of potash by occlusion or adsorption by the precipitated barium phosphate.

This loss may be obviated by using calcium oxide instead of barium hydroxide to remove the phosphoric acid.

The following method is one somewhat improved by the writer from a method in official use in Holland, and is applicable to all mixed fertilisers containing potash salts :—

10 g. of the sample are gently incinerated, placed in a 500 ml. flask and warmed with 10 ml. hydrochloric acid, gradually diluted with water to about 300 ml. and boiled. 10 g. of pure lime (made by calcining pure $CaCO_3$ in a muffle) are made into a cream with water and poured into the flask which is gently boiled and heated in a water-bath for ½ hour with frequent shaking. The flask is cooled and made up to 500 ml. The contents are filtered and 250 ml. are placed in another 500 ml. flask and made acid with hydrochloric acid, boiled and barium chloride added sufficient to precipitate all sulphuric acid. The liquid (without filtration) is then made alkaline with ammonia and the calcium and excess of barium removed in the usual way with ammonium carbonate and a little oxalate. After cooling and making up to the mark, the liquid is filtered and 100 ml. evaporated to dryness. The ammonium salts are expelled in the usual way by the use of a very low gas flame. The potash is then determined by the perchlorate method as previously described in the official method.

DETERMINATION OF NITROGEN IN FERTILISERS.

This is effected by the wet combustion method which bears the name of its inventor, Kjeldahl, although it has been variously modified.

In absence of nitrates (which must first be ascertained) the method commonly in use and prescribed by the Ministry of Agriculture for use under the Fertilisers and Feeding Stuffs Act is the modification known as the Kjeldahl-Arnold-Gunning method, being as follows :—

A weighed portion of the sample is placed in a Kjeldahl digestion flask with 25 ml. (or more if necessary) of concentrated sulphuric acid and a globule of mercury or a small crystal of copper sulphate. The contents are gently heated until frothing ceases, when 10 g. of potassium or sodium sulphate (anhydrous) are added and the flask further heated until the colour of the clear liquid ceases to diminish. The digestion is then further continued for at least another hour. (With some materials such as hoof and horn yet another hour's digestion is desirable.) The contents of the flask are washed into a distillation flask and the ammonia determined by distillation into standard acid after liberation by sodium hydrate solution. When mercury has been used, a small quantity of sodium sulphide is added—after the introduction of the sodium hydrate solution—to decompose any mercurammonium compounds formed during the digestion.

When nitrates are present in conjunction with organic and ammoniacal nitrogen the method prescribed is the Kjeldahl-Arnold-Gunning-Jodlbaur method.

A weighed portion of the sample is treated in a Kjeldahl digestion flask with 30 ml. of concentrated sulphuric acid containing 1 g. of salicylic acid or 1 g. of phenol, the flask being shaken so as to mix its contents without delay. (It is preferable to hold the flask immersed in ice water.) The shaking is continued at intervals during 10 minutes, the flask being kept cold and then 10 g. of potassium or sodium sulphate (anhydrous) are added together with either 5 g. of crystalline sodium thiosulphate or 2 g. of zinc dust. The operation is then conducted as already described for samples containing no nitrate.

The rationale of the process is that the nitric acid when liberated by the sulphuric acid forms a nitro-compound with the phenol or salicylic acid which is subsequently reduced and finally yields ammonia.

The method works accurately except when the fertiliser contains a substantial quantity of potassium or sodium chloride. In the case of a fertiliser containing superphosphate, organic nitrogen, ammonium sulphate and potassium or sodium nitrate and commercial sulphate of potash, the results are accurate. But if the fertiliser contains a substantial admixture of potassium chloride or of a low grade potash salt containing much sodium chloride, the method unfortunately entails some loss of nitrogen by the evolution of $NOCl$, and the figure obtained for nitrogen in such cases may be substantially too low.

In such cases the writer has found that correct results are obtainable by combining the Devarda method (which is described later in its application to the analysis of nitrates) with the Kjeldahl method in one operation, as follows (*see* Dyer and Hamence, Analyst, 1938, **63**, 866–870):—

About 2 g. of the sample and 3 g. of finely powdered Devarda metal are placed in a 500 ml. Kjeldahl digestion flask, and the sides of the flask washed down with 50 ml. of water. The flask is closed with a rubber stopper provided with (*a*) a tap funnel, (*b*) a delivery tube connected with a U-tube (with bulbs) containing 10 ml. of 10% sulphuric acid. 5 ml. of sodium hydroxide solution of 1·40 sp.gr. are added through the tap funnel. The flask is allowed to stand for ½ hour and then heated to just short of the boiling-point for a further hour.

At the end of this digestion the flask is cooled and 20 ml. of sulphuric acid of 1·50 sp.gr. are added through the tap funnel in such a manner that the sides of the Kjeldahl flask are washed down by the acid. The rubber stopper is removed and the contents of the U-tube are washed out into the Kjeldahl flask.

25 ml. of concentrated sulphuric acid are added to the flask and the flask heated until all the water has boiled off. 10 g. of sodium sulphate are added and the flask heated until the colour of the clear liquid ceases to diminish and for 2 hours thereafter. The operation may be accelerated by the addition of a globule of mercury. The ammonia is then distilled off as in the Kjeldahl method.

Special Modifications for Calcium Cyanamide.—In the case of calcium cyanamide (free from nitrate) the Kjeldahl-Arnold-Gunning method requires a slight modification. If the calcium cyanamide is treated with strong sulphuric acid, as in the case of other fertilisers, it is well established that there is a loss of nitrogen. In dealing, therefore, with this material, the sulphuric acid (25 ml.) must be first diluted with an equal volume of water and the digestion (with a drop of mercury) continued as usual. There is then no loss of nitrogen.

In the case of calcium cyanamide in which nitrate has been incorporated (*see* p. 65) the ordinary Jodlbaur method is not available, owing to the necessity for dilution of the sulphuric acid for getting the whole of the cyanamide nitrogen; while if the acid is diluted there is, on the other hand, a loss of nitric nitrogen, as this cannot be "fixed" by the phenol or salicylic acid except in strong sulphuric acid.

It is found, however, that the combined Devarda-Kjeldahl method (Dyer and Hamence), already described, gives accurate results for the total nitrogen in this mixture of calcium cyanamide and nitrate.

Determination of Nitrogen in Sodium or Potassium Nitrate.—This may be effected by the Devarda method or by the Ulsch method, which methods are prescribed as alternatives in the regulations of the Ministry of Agriculture (1932) The former is preferred by the writer. It is best carried out as follows: 5 g. are dissolved in 500 ml. of water and 100 ml. (=1 g. of sample) are placed in a distillation flask with not less than 6 g. of powdered Devarda metal, diluted with about 300 ml. of water. An excess of concentrated sodium hydroxide solution is then added and the flask is immediately connected with a distillation apparatus, allowed to stand for at least ½ hour, slowly heated and the resulting ammonia distilled off and collected in the usual way.

In the Ulsch method a measured quantity of a solution of the nitrate equivalent to 1 g. is placed in a ½ litre Erlenmayer flask with 10 g. of reduced iron and 20 ml. of sulphuric acid of sp. gr. 1·35. The flask is closed with a rubber stopper provided with a thistle-headed funnel containing glass beads, and allowed to stand until effervescence ceases, after which it is boiled for 5 minutes; and after removing the flask any liquid on the beads in the funnel is rinsed with water into the flask, the contents of which are again boiled for a few minutes and the beads again washed with water. The contents of the flask are then mixed with excess of soda and the ammonia distilled off in the usual way.

A disadvantage of the Ulsch method is the very usual presence of an appreciable quantity of nitrogen in reduced iron which is apt to be irregularly distributed so that even the usual precaution of a " blank experiment " may sometimes fail to secure an accurate result. It is mainly owing to the difficulty often experienced of getting reduced iron containing a minimum of nitrogen that the writer has been led to prefer the Devarda process.

General Observations on Nitrogen Determination.—The quantity of material operated upon for the determination of nitrogen will vary according to its nature. In the case of materials rich in nitrogen, from 1 g. to 1·5 g. may be used. On the other hand, in the case of materials composed chiefly in organic matter, and containing only small quantities of nitrogen—like low quality dissolved bone compounds—as much as 5 or 6 g. may be conveniently operated upon. It is usually convenient to make two simultaneous experiments on different quantities of the material, such as 1 g. and 1·5 g., or 1·5 g. and 2 g. The larger the quantity of material that can be satisfactorily dealt with, the less, obviously, is the multiplication of experimental error. Duplicate results, in careful hands, should differ by no more than a few units in the second place of decimals, when expressed as percentage of nitrogen in the material under examination.

It is important that all the materials used in any of the methods described must be examined as to their freedom from nitrogen, by means of a control experiment carried out under similar conditions with the same quantities of the reagents which are employed in the actual analysis, 1 g. of pure sugar being substituted for the weighed portion of the sample. The quantity of standard acid neutralised in the control experiment—which should be small if the materials are good—must be deducted from the total quantity of acid found to have been neutralised in the distillation of the sample. The observance of this precaution is of vital importance, seeing that small quantities of nitrogen compounds are sometimes found even in sulphuric acid sold as pure for analysis; while traces of nitrates or nitrites may be present in sodium hydroxide.

In the case of ammonium sulphate or other material containing nitrogen in the form of ammonium salts only (other than ammonium nitrate), the nitrogen may be determined by simple distillation with alkali.

Lime.—In lime for agricultural use the regulations of the Ministry (1932) at present in force direct that the free lime (calcium oxide) shall be estimated as follows :—

The sample is rapidly ground and passed through a sieve having apertures of 0·2 mm. square. 5 g. of the powdered sample thus prepared are placed in a litre bottle moistened with 10 ml. of neutral alcohol (to lessen possibility of caking); 490 ml. of a 10% solution of cane sugar (neutral to phenol phthalein) are added, and the bottle agitated in a shaking apparatus for not less than 4 hours. The solution is then filtered and an aliquot part titrated with semi-normal hydrochloric acid, using phenol phthalein as indicator.

This method does not take into account any lime present as carbonate (which should also be determined and stated separately) and also ignores that portion of the lime which, in lime burnt from silicious limestone, remains after burning in loose combination with silica and easily neutralises dilute acids. Such lime may be less rapidly available than free lime, but is not without agricultural value.

General Observations as to Preparing Samples for Analysis.—In the case of all samples, whether of fertilisers or of raw materials for use in their manufacture, it is obviously important to obtain a thoroughly representative portion for analysis.

To this end it is usual, in the case of powdered fertilisers in dry or moderately dry condition, to pass the sample through a sieve, the perforations of which are about 1 mm. in diameter, pulverising the portions at first retained on the sieve—either in a mortar or, better, in a suitable mill—until they pass through. Adventitious materials which cannot be conveniently crushed, such as fragments of metal sometimes found in basic slag, must be removed and weighed, and subsequently allowed for in calculating the results of the analysis.

Some materials, like shoddy, wool waste, or hair, cannot be powdered, but as a rule they can be passed through a shredding machine; or, if this is not possible, they must be finely cut up by hand.

Some moist fertilisers also do not admit of being passed through a sieve, and in dealing with these the analyst must use his discretion as to the best mode of obtaining an average sample.

In the case of many moist materials, especially fibrous materials like shoddy or wool waste, or guano, moisture is inevitably lost during the preparation of the sample. It is therefore necessary to determine the moisture separately in a large average portion of the original material before proceeding to pulverise the remainder. The moisture must also be determined in the fine material as prepared for analysis, and the results of the analysis recalculated so as to represent the percentages present in the sample in its original moist condition.

Crystalline or saline materials, like ammonium sulphate, potassium chloride, kainit or sodium nitrate, are best prepared by mixing and rapidly grinding in a stoneware mortar, the portion reserved for analysis being especially finely ground.

In the case of raw mineral phosphates, it is usual to determine the moisture in a rough sample separately taken for this purpose, and to conduct the rest of the analysis on a separately prepared fine portion, after drying the latter at 100°—the results being returned on the dry basis, with a simple statement at the foot of the analysis of the percentage of moisture in the rough sample.

But in the case of almost all other materials, the results of the analysis are returned as percentages of the material in its original moist condition.

B. D.

"*FESEMCO*" slate (Vol. IV, 117*c*).

FETTBOL (Vol. II, 26*c*).

"*FIBERLOID*" (Vol. II, 443*b*, 480*a*).

FIBRES, ANIMAL, SILK. Silk is a solidified secretion produced by the larvæ of numerous species of moths, all of which are members of the natural order *Lepidoptera*. The most important of these silk spinners are *Bombyx mori* (mulberry worm), *Bombyx textor*, *Bombyx sinensis* (Chinese monthly worm), *Bombyx croesi* (hot weather worm), *Bombyx fortunatus* (cold weather worm), *Antheræa mylitta* (Tussah silk worm), *Antheræa pernyi* (which yields Shantung silk), *Attacus ricini* (which yields Eria silk), and *Attacus cynthia*. Most of the *Bombyx* moths are domesticated or bred under controlled conditions, with the object of producing the best type of silk, known as true silk, whereas the *Saturnidæ* are not cultivated to the same extent and consequently yield a less valuable product, known as wild silk. The latter, although generally brown in colour and coarser and stiffer than true silk, has increased in importance during recent years owing to advances in the technology of processing. The fibre obtained from *Bombyx mori*, which feeds on the leaves of the mulberry tree (*Morus alba* or *Morus rubra*), is usually taken as the standard for true silk, and unless otherwise stated, the term silk used in this article refers to this standard product.

Great care is exercised in the rearing of silkworms and much research has been carried out to determine the optimum conditions for the larvæ. It has been found (Nakahama and Nishimura, Bull. Agric. Chem. Soc. Japan, 1937, **13**, 45, 79) that atmospheres of high relative humidity tend to cause a reduction in the quality and amount of silk produced, and that excessive feeding, although resulting in larger and heavier cocoons, has a similar deleterious effect upon the quality of the silk. Conditions in the silk worm establishments or filatures must be carefully controlled if the best results are to be obtained, especially as the larvæ are subject to a considerable number of diseases, some of which are highly contagious, *e.g.* pébrine, flacherie, grasserie and muscardine. The silkworm is hatched in the larval form from eggs laid by the moth, and after feeding voraciously for 32–38 days, during which time it changes its skin four times, passes into the pupal stage. As a means of protection from external agencies, the insect spins a cocoon round its body by ejecting the contents of its two silk glands through minute spinnerets, one on each side of the head. By this means, two filaments or brins, composed of a protein known as fibroin and cemented together with sericin, a compound similar in constitution but different in properties, are produced. This composite raw silk thread, which solidifies on emerging into the air, is termed the bave.

There is considerable controversy as to the exact method by which these threads are produced, and the topic has recently been comprehensively reviewed by Bergmann (Text. Res. 1939, **9**, 329). According to early workers on silk formation, sericin is produced by atmospheric oxidation of fibroin, which is the sole product of the glands, but this hypothesis was shown to be false by the application of a staining technique which demonstrated the presence of sericin in the silk producing organs. Most investigators are agreed that fibroin is produced in the posterior portion of the gland, but there is some difference of opinion regarding sericin formation. Certain authors (Blanc, Rapp. Lab. d'Études de la Soie, Lyon, 1887–88, **4**, 52; Tanaka, J. Coll. Agric. Tôkohu Imp. Univ. 1911–12, **4**, 145) believe that this protein is produced by the interglandular oxidation of fibroin, whilst others (Lidth de Jeude, Zool. Anz. 1878, **1**, 100; Raulin and Sicard, Rapp. Lab. d'Études de la Soie, Lyon, 1886, **3**, 43; Machida, J. Coll. Agric. Tokyo, 1937, **9**, 119; Proc. Imp. Acad. Tokyo, 1926, **2**, 421) provide evidence supporting the theory that sericin and fibroin are secreted as completely independent compounds in the middle and posterior portions of the gland, respectively. Silk is present in these organs as a viscous liquid, and is quite different in properties from cocoon silk. The mechanism by which solidification is effected is rather obscure, but the most satisfactory theory appears to be that due to Foa (Kolloid-Z. 1912, **10**, 12), who is of the opinion that the change is produced purely by the mechanical action of stretching and pulling to which silk is subjected after leaving the gland. Confirmation of this hypothesis has been provided by Hirazuka (Bull. Imp. Sericult. Exp. Sta. Nakano, 1918, **1**, 203), Hirasawa (Bull. Sericult. and Silk Ind. Japan, 1930, **3**, 6) and Ongaro (Giorn. chim. ind. applicata, 1933, **15**, 506), whilst Ramsden (Nature, 1938, **142**, 1120) has put forward evidence in support of the view that shearing forces contribute towards the solidification.

During the formation of the cocoon, the larva moves its head as though making a figure of eight, and consequently the fibre is fairly easily unwound (reeled) when required for industrial purposes. Although most cocoons are used for silk production, a certain number are retained for purposes of reproduction. These are allowed to develop naturally, but when cocoons are to be employed as a source of silk, it is necessary to kill the insect inside, by heating in an oven at 60–70°C. for 3 hours, or by placing in steam for 10 minutes. If the insect were allowed to live and emerge as an adult moth by softening a portion of the cocoon with an alkaline fluid ejected from its body, there would be a reduction in the length of reelable silk. A filature cocoon of average size weighs from 1 to 3 g. and contains some 3,000–4,000 yards of silk, of which 600–1,200 yards may be reeled. This is worked up as true silk, which consists of long uniform filaments, whilst the unreelable portion and inferior or damaged cocoons, together with those of the wild worms, are manufactured on a system involving carding and spinning.

Composition of Silk.

Raw silk threads, which decrease in diameter as the inside of the cocoon is approached, consist mainly of sericin and fibroin, together with moisture, mineral salts, waxes and colouring matters. The filaments are generally regarded as containing 11% of moisture, 66% of fibroin, 22% of sericin and 1% of mineral and colouring matters (Allen's "Commercial Organic Analysis," 5th ed., Vol. 10, p. 200), although, as shown in

Table I, the exact figures vary according to the type and history of the silk.

TABLE I.

Type of silk (dry).	Fibroin.	Sericin.	Wax and fat.	Salts.
Raw white mulberry .	76·20	22·01	1·36	0·3
Raw yellow mulberry .	72·35	23·13	2·75	1·6

Raw silk varies a great deal in colour. The several types of *Bombyx* worm produce white, yellow or greenish yellow silk, and the wild varieties yield a product which may be light or dark brown, golden yellow or green. Natural colouring matters in silk have therefore been divided by W. Bergmann (Text. Res. 1939, **9**, 397), into yellow, green and brown. The first are attributed to the presence of xanthophyll (*v.* Vol. II, 399*c*), carotene (*q.v.*) in various oxidised forms, and violoxanthin (*v.* Vol. II, 399*d*). Xanthophyll (lutein) was first isolated in a crystalline state by Oku (Bull. Agric. Chem. Soc. Japan, 1929, **5**, 81 ; 1932, **8**, 7, 89 ; 1933, **9**, 91) who estimated that normal yellow silk contained 0·022–0·024%. The same author was also successful in isolating lutein from mulberry leaves (*ibid.*, 1930, **6**, 104). Certain of the green pigments have been shown (Jucci and Manunta, Atti R. Accad. Lincei, 1932, [vi], **15**, 473; Boll. Soc. Ital. Bio. sperim. 1932, **7**, 162, 163. Manunta, Atti R. Accad. Lincei, 1933, [vi], **18**, 513 ; Mem. Accad. Lincei, mat. nat. 1935, [vi], **6**, 101) to be closely related to the flavones, and others, obtained from some wild silks, resemble chlorophyll (Gautier, Compt. rend. Soc. Biol. 1906, **61**, 419, 696 ; 1907, **62**, 234. Oku, Bull. Agric. Chem. Soc. Japan, 1934, **10**, 158, 164). Oku (*l.c.*) succeeded in identifying a flavone which he termed *bombycin*, and which on hydrolysis with 5% sulphuric acid, yields, in equimolecular proportions, glucose and an aglucone, *bombycetin* ($C_{20}H_{19}O_7N$), m.p. 170–180°C. Brown pigments differ from yellow and green, in that they do not become evident until the completion of the cocoon. Blanc (Rapp. Lab. d'Études de la Soie Lyon, 1886, **3**, 65), Levrat and Conte (*ibid.* 1901–02, **11**, 53). Dewitz (Arch. Entw.-Mech. Org. 1910–11, **31**, 617 ; Zool. Anz. 1904, **27**, 161), and others have shown that cocoons of *Antheræa mylitta, Attacus orizaba, Attacus pernyi, Saturnia pyri* and *Saturnia pavonia* change from white to brown 24–48 hours after completion, and attribute this to the fact that the worm covers the whole surface of the cocoon with a fluid ejected from the anus. The composition of the brown pigments is somewhat obscure, but Przibram and Schmalfuss (Biochem. Z. 1927, **187**, 467) have separated pure 3 : 4-dihydroxyphenylalanine (dopa) from cocoons of *Samia cecropia* and have proved that this chromogen is responsible for the development of the brown colour of wild silk cocoons.

Cocoon wax is considered to be unevenly distributed throughout, as the amount of extractable wax decreases from the external to the internal layers (W. Bergmann, Text. Res. 1938, **8**, 195, 221). Quantities of this material extracted from raw silk are conveniently expressed in terms of the ether-soluble number (E. S. number) which has been defined by Bergmann (*ibid.* 1939, **9**, 175) as the number of milligrams of ether-soluble material contained in 10 g. of silk. Values of this characteristic vary from 30–100, according to the type of silk, those for white Japanese and Chinese silks lying between 40 and 60, and those for yellow silks of Japanese and Italian origin between 90 and 100. No apparent relationship exists between the E. S. number and the nature, boil-off, tenacity, elongation, cohesion or resistance to friction of the raw silk filaments, but there is a direct connexion between E. S. number and the wettability of the fibre, a fact which is of considerable technical importance. The composition of the wax is not very well defined, but extraction of raw Chinese silk by means of solvents yields a light brown wax of m.p. 50–60°C., which may be resolved into a mixture of primary alcohols ($C_{26}-C_{32}$), fatty acids ($C_{26}-C_{32}$), paraffins ($C_{25}-C_{31}$), and liquid fatty acids. This wax approximates very closely to that obtained by Chibnall and his co-workers from certain plant cuticles, a fact which adds support to the view that silk wax is derived from the comparatively large amounts of plant waxes consumed by the larvæ.

The chief components of raw silk, sericin and fibroin, are proteins composed of carbon, nitrogen, hydrogen and oxygen, in the proportions indicated in Table II.

TABLE II.

Protein.	Carbon.	Hydrogen.	Nitrogen.	Oxygen.	Reference.
Fibroin	48·53	6·43	18·33	26·67	Matthews, "Textile Fibers," 4th ed. 1924—mean of several determinations.
Sericin	42·60	5·90	16·50	35·00	Matthews, *op. cit.* p. 301.]

As distinct from the keratins, sericin and fibrion contain no sulphur, and, in consequence, silk has properties markedly different from those of wool and hairs.

Sericin.—Sericin, which is a yellowish, transparent substance, may be removed from the raw fibre by boiling in alkaline soap solutions, the loss in weight resulting from such treatment being known as the boil-off. The quantity of material removed varies with the type of silk from 18–25%, as is evident from Table III.

As a result of degumming, the bave is separated into two brins which are composed of practically pure fibroin, and are much softer and more lustrous than raw silk. Pure sericin may be prepared by boiling raw silk in water for several hours, and subsequently precipitating the soluble protein with lead acetate. An alternative procedure consists in precipitating sericin from the aqueous solution by means of acetic acid, wash-

TABLE III.

Silk.		% Loss in weight.
Yellow—	French	24·18
	Italian	23·40
	Piedmont . . .	22·92
	Spanish	24·94
	Syrian	24·35
	Bengal	22·09
White—	French	21·54
	Piedmont . . .	20·68
	Italian	21·40
	China	17·98
	Canton	22·17
	Japanese . . .	17·90

Reference.—Matthews, "Textile Fibers," 4th ed. 1924, p. 292.

TABLE IV.

Amino acid.	From Canton silk.[1]	From Indian Tussah silk.[2]	From silk of a bivoltine species of worm.[3]	From *Bombyx mori* silk.[4]
	%	%	%	%
Glycine . .	1·2	1·5	3·9	—
Alanine . .	9·2	9·8	3·5	—
Leucine . .	5·0	4·8	0·4	1·69
Serine . .	5·8	5·4	5·9	6·81
Aspartic acid	2·5	2·8	3·9	—
Glutamic acid	2·0	1·8	0·8	—
Phenylalanine	0·6	0·3	0·5	—
Tyrosine . .	2·3	1·0	3·2	5·69
Proline . .	2·5	3·0	0·4	—
Arginine . .	—	—	—	4·56
Lysine . .	—	—	—	1·69
Histidine .	—	—	—	1·02

[1] Abderhalden and Worms, Z. physiol. Chem. 1909, **62**, 142.

[2] Strauch, *ibid.* 1911, **71**, 365.

[3] Inouye and Hirasawa, J. Tokyo Chem. Soc. 1918, **39**, 300.

[4] Türk, Z. physiol. Chem. 1920, **111**, 69.

ing with water, and finally treating with cold alcohol, boiling alcohol, and ether in succession. An empirical formula $C_{15}H_{25}O_8N_5$ has been assigned to sericin by Cramer (J. pr. Chem. 1865, [i], **96**, 91), who expressed the relationship between this protein and fibroin by the following equation:

$$\underset{\text{Fibroin.}}{C_{15}H_{23}O_6N_5}+H_2O+O=\underset{\text{Sericin.}}{C_{15}H_{25}O_8N_5}$$

Sericin, which is soluble in hot water, hot soap solution, and dilute caustic alkalis, may be precipitated from aqueous solution by the addition of alcohol, tannin, basic lead acetate, stannous chloride, bromine or iodine. Formaldehyde is capable of rendering sericin insoluble in hot water and soap solutions, and if raw silk is treated with this reagent, the sericin becomes more firmly attached to the fibroin. A similar fixation may be effected by the use of chromium salts, which cause the fibres to assume a wool-like appearance. The amino groups of the protein appear to play a part in this reaction, since deaminated sericin absorbs less chromium than does the unmodified material (Oku and Hirose, Bull. Agric. Chem. Soc. Japan, 1937, **13**, 1257; J. Agric. Chem. Soc. Japan, 1938, **14**, 178, 309). By boiling in acid solutions sericin may be hydrolysed into a mixture of amino acids. Although, as shown in Table IV, the results of analyses on such hydrolysates are widely divergent and inadequate, it is evident that alanine and serine are important constituents.

In common with other proteins, sericin combines with dilute acids and alkalis and possesses an isoelectric point. Older values of this characteristic are of an approximate nature only (Kodama, Biochem. J. 1926, **20**, 1208; Denham and Brash, J. Text. Inst. 1927, **18**, T520), but a recent investigation by Harris (Text. Res. 1939, **9**, 374) has provided the more accurate figure of p_H 4·3. The determination was carried out by measuring the electrical mobility of sericin absorbed on glass particles of 0·1–2 microns in diameter, and acetate buffers were employed to minimise specific ion effects. On account of its high molecular weight, sericin forms a colloidal solution in water. The properties of such solutions have been investigated with great thoroughness by Kaneko (Bull. Chem. Soc. Japan, 1934, **9**, 207, 241, 283, 344, 409, 461, 600), who has provided accurate data for the viscosity, specific conductivity, surface tension, cataphoretic velocity, and the variation of these characteristics with temperature and other factors. Sericin solutions are excellent emulsifying agents, and show a protective colloid capacity, as revealed by the gold number of 0·02–0·38. Coagulation is effected by the addition of heavy metal salts or organic solvents such as alcohol, acetone or benzene.

By suitable treatment of sericin solutions, different fractions, which have been designated as sericin A and sericin B, may be obtained. The separation may be effected in a number of ways. The method of Mosher (Amer. Dyestuff Rep. 1932, **21**, 341) consists in adjusting the p_H of the solution to 3·6–3·8, when sericin B is precipitated, followed by the addition of alcohol to deposit the A variety. Kaneko (*l.c.*), however, has shown that the two forms may be prepared by mixing a luke-warm sericin solution with an equal volume of saturated ammonium sulphate, or by freezing the solution for several hours and then allowing it to return slowly to room temperature. Under these conditions sericin A may be separated, while sericin B remains in solution and may be isolated in the usual manner. There is some doubt (Matsunaga, J. Soc. Chem. Ind. Japan, Suppl. binding, 1936, **39**, 465) as to the identity of the various fractions separated by different workers, but all are agreed that whilst the two forms of sericin exhibit the usual protein characteristics, they are quite different in many chemical and physical properties.

The more important differences between the sericins identified by Kaneko (*l.c.*) may be summarised as follows:

(1) Sericin A yields more viscous solutions than does B.

(2) Sericin B is more soluble than A in distinctly acid and alkaline solutions.

(3) Sericin A is coagulated by strong solutions of ammonium sulphate and by electrodialysis, whilst sericin B remains in solution as a result of such treatments.

(4) After freezing a solution containing both forms, sericin A cannot return to the colloidal state, whilst B again enters into solution.

(5) The two varieties have different isoelectric points, although the reported values vary somewhat. Thus, two results for the isoelectric point of sericin A are 3·8 and 4·1, whilst the corresponding figures for sericin B are 4·5 and 4·3.

(6) The specific gravities of sericins A and B are 1·356 and 1·309, respectively.

(7) Sericin A has the greater protective colloid action, as shown by its gold number being less than that of sericin B.

(8) Sericin A has a greater affinity for dyes than has B.

(9) Differences in composition are evident from the following figures:

Sericin A.—Total nitrogen—16·36%, Tyrosine—2·62%, Glycine—6·18%.

Sericin B.—Total nitrogen—16·11%, Tyrosine—5·35%, Glycine—4·89%.

The two varieties isolated by the method of Mosher exhibit similar differences in physical and chemical properties, but there are more data regarding their constitution. The nitrogen content of sericin A has been shown (Ito, J. Agric. Chem. Soc. Japan, 1937, **13**, 1201) to be 17·37% and that of B, 16·88%, whilst the distribution of nitrogen in the two forms is given in Table V (Ito, *ibid.* 1939, **15**, 50).

TABLE V.

Type of nitrogen.	Sericin A.	Sericin B.
Amide	12·14	10·22
Humin	0·17	0·90
Cystine	0·00	0·00
Arginine	9·15	9·68
Lysine	4·70	4·72
Histidine . . .	2·71	3·80
Monoamino . . .	70·10	69·19

In addition, sericin A contains 0·45% of sugars and 0·37% of amino sugars, and sericin B 1·08% and 1·27% of these compounds. When both varieties are heated with water, a considerable amount of ammonia is liberated, the greater quantity being obtained from sericin A.

TABLE VI.

Origin of Fibroin.	% of amino acids.								
	Glycine.	Alanine.	Leucine.	Serine.	Aspartic Acid.	Glutamic Acid.	Phenylalanine.	Tyrosine.	Proline.
From New - Chwang silk (Abderhalden and Rilliet, Z. physiol. Chem. 1909, **58**, 337).	19·7	23·8	1·6	1·0	2·9	1·7	1·2	9·8	1·85
From Canton silk (Abderhalden and Behrend, *ibid.* 1909, **59**, 236)	37·5	23·5	1·5	1·5	0·75	Not detected	1·6	9·8	1·0
From Shantung Tussah silk (Abderhalden and Brahm, *ibid.* 1909, **61**, 256) . .	14·5	22·0	1·0	1·8	1·0	1·75	1·0	9·7	2·5
From Bengal silk (Abderhalden and Sington, *ibid.* 1909, **61**, 259)	30·5	20·0	1·2	1·75	0·8	trace	1·4	10·0	1·0
From Niĕt ngō tsam silk (Abderhalden and Brossa, *ibid.* 1909, **62**, 129) . .	24·0	18·5	1·2	1·5	2·0	3·0	1·0	7·8	1·2
From Indian Tussah silk (Abderhalden and Spack, *ibid.* 1909, **62**, 131) . .	9·5	24·0	1·5	2·0	2·5	1·0	0·6	9·2	1·0
From Tsai-tsao-tsam silk (Abderhalden and Schmid, *ibid.* 1910, **64**, 460) . .	25·2	18·2	0·9	1·2	2·1	2·0	1·0	7·8	1·0
From Chefoo silk (Abderhalden and Welde, *ibid.* 1910, **64**, 462)	12·5	18·0	1·2	1·0	2·0	2·0	1·0	8·5	2·5

A third fraction, sericin C, has also been isolated by Mosher (Amer. Silk and Rayon J. 1934, **53**, April, 43) from the last portion of sericin which can be removed from raw silk. The protein is insoluble in all common solvents, is resistant to enzyme action, and has little ability to emulsify oils and fats. It is very doubtful whether this substance is a true sericin, and consequently, it has also been classified as a protein intermediate in properties between sericin and fibroin.

Fibroin.—The second protein constituent of silk, fibroin, is insoluble in water and organic solvents, but dissolves in concentrated solutions of mineral acids, alkaline hydroxides, or certain salts, and in ammoniacal solutions of copper or nickel oxides. On hydrolysis by means of strong acids, various amino acids have been isolated, the most important being glycine, alanine and tyrosine. Investigations by Abderhalden in the years 1909 and 1910 indicate that fibroins obtained from various types of silk differ in composition (*see* Table VI on previous page and Z. physiol. Chem. *l.c.*)

Later, Abderhalden (*ibid.* 1922, **120**, 207) published the following figures for the percentage composition of hydrolysates obtained from the fibroin of *Bombyx mori* silk; glycine 40·5, alanine 25, tyrosine 11, leucine 2·5, serine 1·8, arginine 1·5, phenylalanine 1·5, proline 1·0, lysine 0·85, and histidine 0·75. More detailed experiments (*ibid.* 1932, **207**, 141; **210**, 246) by the same author revealed the presence of norvaline, valine, chitosamine, aspartic acid, glutamic acid and glucuronic acid, in addition to the previously mentioned compounds. By treating fibroin with normal caustic soda solution at 37°C. for 40 hours, a pentapeptide, glycylserylprolyltyrosylproline, and a tetrapeptide, serylprolyltyrosylproline, were isolated. The most recent values for the composition of hydrolysates obtained from silk fibroin are due to Bergmann and Niemann (J. Biol. Chem. 1938, **122**, 577), who have developed new methods for the determination of glycine and alanine, and have provided new figures for the amounts of tyrosine, glycine, alanine and arginine. Their results, together with older values for other amino acids, are summarised in Table VII.

TABLE VII.

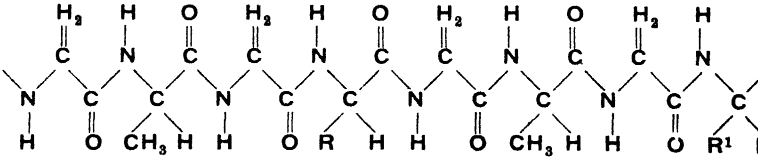
Amino acid.	Percentage.	Reference.
Glycine	43·8	Bergmann and Niemann (*l.c.*).
Alanine	26·4	do.
Tyrosine	13·2	do.
Arginine	0·95	do.
Lysine	0·25	Vickery and Block (J. Biol. Chem. 1931, **93**, 105).
Histidine	0·07	do.
Leucine	2·5	Abderhalden (*l.c.*).
Serine	1·8	do.
Proline	1·0	do.
Phenylalanine	1·5	do.

The amino acid composition of the protein hydrolysate is therefore comparatively well established, and on the basis of this analysis, Bergmann and Niemann calculated a minimum molecular weight of 217700. They have also suggested that a portion of the fibroin molecule is built according to the following plan:

—G—A—G—T—G—A—G—Ar—G—A—G—X—G—A—G—X—
(—G—A—T—G—A—G—X—G—A—G—X—G—A—G—X)$_{12}$—
G—A—G—T—G—A—G—X—G—A—G—X—G—A—G—Ar—
(G—A—G—T—G—A—G—X—G—A—G—X—G—A—G—X)$_{13}$—,

where **G** denotes glycine, **A** alanine, **T** tyrosine, **Ar** arginine and **X** any other aminoacid residue.

The configuration of the fibroin molecule has also been the subject of many physical investigations. As a result of the application of X-ray technique it has been established that this protein is composed of an amorphous mass containing embedded crystallites, which consist of long, fully extended polypeptide chains, lying closely side by side to form long, thin, crystalline bundles or micelles, oriented parallel to the length of the fibre. The chains are formed by linking together α-amino acids, mainly glycine and alanine, as follows:



The effective length of each amino acid residue in such a system is 3·5A, whilst the distance of separation between the parallel peptide chains lies somewhere between 4·4 and 6·1A, and the pattern repeats in the direction of the fibre axis at a distance of 6·95±0·25A, which corresponds to the length of two amino acid residues (Meyer and Mark, Ber. 1928, **61** [B], 1932; Kratky and Kuriyama, Z. physikal. Chem. 1931, *B*, **11**, 363; Brill, Annalen, 1923, **434**, 204). Calculations based on these values and on the formula set out by Bergmann show that the macromolecules of silk fibroin are approximately 900 millimicrons in length, but Alexander (Ind. Eng. Chem. 1939, **31**, 630), as a result of experiments with the ultramicroscope, believes them to be considerably smaller.

The Japanese worker, Kaneko, has demonstrated (J. Agric. Chem. Soc. Japan, 1936, **12**, 101, 800; 1937, **13**, 208, 1125) that silk fibroin may be fractionated into fibroin A and fibroin B, by precipitation under carefully controlled conditions, from a dispersion in cold concentrated hydrochloric acid. The A variety has the higher specific gravity, tyrosine content and isoelectric point, and is more resistant to chemical reagents, although it is more readily stained by acid colours. Both forms give positive results with the xanthoproteic reaction and Millon's reagent, the coloration being more intense in the case of fibroin A.

Since fibroin is a typical protein, it is capable of benzoylation and acetylation, and these reactions proceed easily. When acetylated with keten, or acetic anhydride, however, much more of the reagent is absorbed than can be accounted for in terms of the hydroxyl and amino groups in the molecule (Carr, Text. Res. 1936, **7**, 103; 1938, **8**, 125, 390). The protein also combines with acids and alkalis, to an extent which is dependent upon the p_H of the medium. Jordan Lloyd and Bidder (Trans. Faraday Soc. 1935, **31**, 864) have pointed out that under their experimental conditions, silk fibroin possesses an isoelectric region from approximately p_H3 to p_H8 in which no combination occurs, but many other workers have been concerned with the more precise determination of an isoelectric point. The methods adopted have been many and varied, and the results widely divergent, as is evident from Table VIII.

The last mentioned determination is probably the most accurate, and consequently, the isoelectric point of silk fibroin may be considered to be 3·6. This figure applies to fibroin from *Bombyx mori*, but it is likely that the position of the isoelectric point is characteristic of each kind of silk (Elöd, *l.c.*). Denham and Brash (*l.c.*), on the other hand, did not find any conspicuous difference between the isoelectric points of samples of Chinese and Italian silks, or even between those of mulberry fibroin and Tussah fibroin. Such an observation, however, is not in agreement with that of Bito (Bull. Sericult. Japan, 1931, **4**, No. 2, 2), who has reported the value of p_H 2·85 for the isoelectric point of Tussah fibroin, but the whole question of the isoelectric point of fibroin is greatly confused by the lack of accurate data.

TABLE VIII.

Investigator.	Method.	Isoelectric Point (p_H).
Denham and Brash (J. Text. Inst. 1927, **18**, T520).	Fixation of metallic and acidic radicals.	3·8
Meunier and Rey (Compt. rend. 1927, **184**, 285).	Swelling in buffer solutions.	4·2
Elöd, Teichmann, and Pieper (Z. angew. Chem. 1927, **40**, 262).	Observations on the effect of fibroin on the hydrogen-ion concentration of conductivity water.	5·1
Hawley and Johnson (Ind. Eng. Chem. 1930, **22**, 297).	Electrophoresis of aqueous suspensions of finely divided fibroin.	isoelectric range, 1·4–2·8
	Flocculation of fibroin suspensions.	isoelectric range, 1·7–2·4
Harris (J. Res. Nat. Bur. Stand. 1932, **9**, 557).	Precipitation of fibroin solutions.	2·1
	Viscosity of fibroin solutions.	2·3
	Electrophoresis measurements.	2·5
Denham *et al.* (Trans. Faraday Soc. 1933, **29**, 300; 1935, **31**, 511).	Swelling.	Minima at p_H, 1·4, 2·8, 3·8 and 4·7.
Rastelli (Kolloid-Z. 1934, **67**, 55).	Fixation of ions from aqueous solutions.	4·6–4·8
Harris (Text. Res. 1939, **9**, 374).	Electrophoretic measurements using refined methods.	3·6

MICROSCOPY OF SILK.

When the raw silk fibre is subjected to microscopic examination, the two brins are clearly visible, and are often quite separate from each other for considerable distances along the fibre, although at other points they adhere closely. The surface of the bave appears irregular, due to broken or torn portions of sericin. This binding layer shows frequent transverse fissures caused by a cracking of the sericin during bending or twisting of the fibre. Degummed silk, which is roughly triangular in cross-section, is much more uniform, and is easily distinguished as a smooth transparent filament of fairly regular diameter, although lumps or swellings are occasionally evident. Striations rarely occur, but when visible are parallel to the fibre axis. Treatment with dilute chromic acid results in the appearance of very fine longitudinal markings. Fibroin may be stained deep red with alloxantin, red with fuchsine, and yellowish brown with iodine, whilst concentrated hydrochloric acid produces a violet colour, and a mixture of sugar and concentrated sulphuric acid stains the fibres rose red, prior to their solution. Both raw and degummed silks exhibit characteristic colours when examined in polarised light, these being most probably caused by the fibroin.

Wild silks may be readily differentiated from the cultivated variety as the fibres are broad and thick, and approximate to a flattened ellipse in cross-section. Tussah silk is characterised by distinct longitudinal striations and peculiar flattened markings, usually running obliquely across the fibre (Matthews, *op. cit.* pp. 270–273, for photomicrographs). By treatment in cold chromic acid, the fibre may be macerated into minute filaments, which according to Höhnel are 0·3–1·5 microns in diameter and are arranged parallel to the length of the fibre. Air canals or spaces between these filaments are probably the cause of coarse longitudinal markings which occur at intervals on the fibre, in addition to the finer striations previously mentioned.

PHYSICAL PROPERTIES OF SILK.

Dry silk has a great affinity for water, and adsorbs water vapour at all humidities, the regain under desorption conditions being always in excess of that under adsorption conditions at the same relative humidity. Owing to the high price of silk it is customary to estimate its moisture content before sale, and a regain of 11% is officially permitted in the case of raw silk. Boiled-off silk appears to have rather less affinity for water, due presumably to the higher adsorptive capacity of the silk gum. Water adsorption data for raw and degummed silks at various temperatures and relative humidities have been provided by Schloesing (Compt. rend. 1893, **116**, 808), Levrat (Rapp. Lab. d'Études Soie, Lyon, 1901, **10**, 39)., Hönig (Text. Forschung, Forschungsheft 3/5, Dresden, 1918), Obermiller and Goertz (Textilber. 1926, **7**, 71; Z. physikal. Chem. 1924, **109**, 145), and Kujirai, Kobayashi and Toriyama (Sci. Papers Inst. Phys. Chem. Res. 1923, **1**, 79). The last authors have also demonstrated that the relationship between the percentage of water adsorbed (Q) and the relative humidity of the atmosphere (H) may be expressed in the form $Q=1/(a/H+b-cH)$ where a, b, and c are constants, whilst the more comprehensive equation $w=(\alpha+\beta\phi)\sqrt[4]{(100-t)}$, where w is the moisture content, ϕ the relative humidity, t the temperature and α and β are constants, is in accordance with the results of Hönig (*l.c.*). The regains of Chinese, Italian and Japanese degummed silks under the same conditions are all similar, according to Denham and Allen (Trans. Faraday Soc. 1933, **29**, 316), but that of Tussah is greater.

The extent of the swelling which occurs when dry degummed silk is exposed to the atmosphere varies with the relative humidity, as illustrated by the results of Denham and Dickinson (*ibid.* 1933, **29**, 300) given in Table IX.

TABLE IX.—MEAN LATERAL SWELLING OF FILAMENTS OF ITALIAN SILK, PER CENT. OF ORIGINAL DRY DIAMETER.

Relative humidity, (%)	20	40	60	80	90	95	100
Mean lateral swelling, (%) .	1·6	2·4	3·5	6·1	8·4	11·1	16·3

A more recent investigation (Ingram, Text. Res. 1938, **9**, 79) has revealed that swelling is also dependent on the diameter of the fibre, since dry filaments of both raw and degummed silk, when placed in water, increase in cross-sectional area in a ratio inversely proportional to their diameters.

The elastic properties of degummed silk vary considerably according to the nature of the silk, but the results of Denham and Lonsdale (Trans. Faraday Soc. 1933, **29**, 305), summarised in Table X, serve to indicate their magnitude.

TABLE X.

All figures relate to tests carried out at 65% R.H.

	Italian silk.	Canton silk.
No. of filaments tested	485	80
Mean diameter (cm.)	0·00130	0·00078 (4)
Breaking load (g.) .	6·8	2·6
Extension at break (% of original length). . . .	25·6	18·4
Tensile strength (dynes per sq. cm. $\times 10^9$)	6·0	6·4
Young's modulus (dynes per sq. cm. $\times 10^{10}$) . . .	7·22	10·74

As in the case of other textile fibres, the relative humidity of the atmosphere and the rate of loading have a great effect on certain of the above values. The results given in Table XI, for example, provide ample evidence of the variation of Young's modulus with relative humidity in the case of degummed Japanese silk filaments.

Recovery of silk filaments after extension takes the form of a rapid contraction followed by a slow creep, and is facilitated by an increase in the relative humidity of the atmosphere. Even in saturated atmospheres, however, the fibres do not regain their original dimensions. This

Table XI.

Relative humidity. %	Young's modulus dynes/cm.^{2}
47·5	$10{\cdot}0 \times 10^{10}$
60	8·9 ,,
70	7·1 ,,
80	6·3 ,,
90	5·1 ,,

statement is illustrated by the figures of Denham and Lonsdale (*l.c.*) given in Table XII.

Table XII.—Recovery of Degummed Italian Silk Filaments about 50 cm. Long after Stretching at 65% Relative Humidity and in Water.

	65% R.H.	In water.
Extension (per cent.) . .	5·00	4·97
Elongation (per cent.)—		
After instant recovery .	2·9	1·39
,, 15 seconds . . .	1·6	1·09
,, 1 minute . . .	1·5	0·99
,, 5 minutes . .	1·3	0·89
,, 1 hour . . .	1·2	0·79
,, 1 day	1·1	0·79
,, 2 days . . .	1·1	—
,, 3 days . . .	1·1	0·79

The density of raw silk lies between 1·30 and 1·37, whereas that of boiled-off silk is lower, values of 1·25 and 1·3 having been recorded (Matthews, *op. cit.*, p. 276). Other physical constants of raw silk include the approximate refractive index n_D 1·595 axial, and n_D 1·538 transverse (Herzog, " Unterscheidung der natürlichen und künstlichen Seiden," Dresden, 1910, p. 75), and a specific heat of approximately 0·33 g.-cal. (Denham and Lonsdale, Trans. Faraday Soc., 1924, **20**, 259).

Finally, the high lustre of degummed silk, its softness, durability, resistance to creasing, and its power of electrical insulation, contribute towards making silk a valuable textile fibre.

Chemical Properties of Silk.

The chemical properties of the raw silk fibre are largely accounted for in terms of the reactivity of sericin and fibroin, whilst the reactions of the commercially degummed material, which have received most attention, are substantially those of fibroin. Warm dilute acids dissolve the sericin, leaving the fibroin unattacked, but with more concentrated acids, especially at higher temperatures, general decomposition occurs. Concentrated nitric acid colours both raw and degummed silk yellow, due to the formation of xanthoproteic acid. Mineral acids in certain concentrations cause the degummed fibres to shrink, a phenomenon which is utilised in the production of silk crêpes. In general, treatment of degummed silk with mineral acids results in a loss of tensile strength, the extent of the degradation depending upon the conditions (Walde and Edgar, Text. Res. 1935, **5**, 460). Organic acids are less destructive and are particularly useful for increasing lustre and scroop. Of especial interest is the union of silk fibroin with tannic acid, which unlike other organic and inorganic acids, cannot be removed easily from the protein by washing with water. As much as 25% of tannic acid may be adsorbed from a hot solution, and considerable amounts are combined in the cold. Alkalis remove the sericin from raw silk, but, if in sufficiently low concentrations, do not seriously attack the fibroin. At higher concentrations, however, the degummed silk loses lustre and tensile strength, due no doubt to hydrolysis of the main chains as in the case of acid decomposition (Walde and Edgar, *l.c.*). Oxidising agents have a destructive effect upon degummed silk, and great care has to be taken when using these compounds in industrial practice. Peroxides appear to produce less degradation than permanganates (Johnson, Walde and Edgar, Iowa State Coll. J. Sci. 1936, **11**, 5), and consequently are preferred for bleaching. On exposure to light, breakdown occurs as a result of oxidative fission of linkings in the silk molecule. Evidence in favour of this view has been provided by Harris (Amer. Dyestuff Rep. 1934, **23**, 215), who exposed skeins of silk to sunlight for 4 months in a vacuum, and in atmospheres of moist and dry oxygen and hydrogen. During this period no deterioration occurred in the skeins exposed in a vacuum or hydrogen, but those in dry oxygen lost about 3%, and those in moist oxygen 10%, of their strength. Silk also readily adsorbs chlorine gas with the formation of chloramines (Trotman, " Bleaching, Dyeing and Chemical Technology of Textile Fibres," Griffin, London, 1925, p. 172), and when moist, is rapidly attacked by ozone.

An interesting property of degummed silk is the ease with which it can be regenerated from solution in various reagents without substantial degradation. The most common solvents are alkaline solutions of copper or nickel hydroxides, concentrated phosphoric or sulphuric acids at low temperatures, liquid ammonia, and concentrated solutions of certain salts, for example, sodium and calcium thiocyanates, sodium iodide, calcium chloride, zinc chloride and magnesium nitrate. Addition of ethylenediamine, di- and tri-ethanolamine, diguanide, amino acids, or poly-hydroxy compounds such as glycerol or glucose, effects a great increase in the rate of solution of fibroin in alkaline copper hydroxide (Takamatsu, J. Soc. Chem. Ind. Japan, Suppl. binding, 1933, **36**, 662, 668; 1934, **37**, 107, 149). Regeneration of silk in the form of a synthetic fibre is of some importance as it provides a means of utilising low quality silk wastes. Solutions of fibroin have also been recommended for the purpose of giving a silk-like finish to cotton goods (Watanabe and Ina, Jap. P. 101826).

Chemical Technology of Silk Processing.

Silk Reeling.—The sorted cocoons are first immersed in hot water, which softens the gum, and the outer portions are then pulled away until a fibre of the required diameter is obtained.

The loose ends of several fibres are brought together by the operator and passed through guides on to the reel to form threads of a suitable size for processing. The product so obtained is termed raw silk or *grège*, and the waste, consisting of short and tangled fibres from the exterior of the cocoons, and of damaged silk, is known as floss silk and is used for the manufacture of spun silk. Raw silk obtained from first-class cocoons is spoken of as *organzine*, and that from inferior cocoons as *tram*. In order to give quantitative significance to the ease with which silk may be reeled from cocoons, the Japanese have introduced the term *kaijo*, which is defined as the weight of raw silk reeled per hour under standard conditions (Kaneko, Bull. Sericult. Japan, 1931, **4**, No. 2, 3). The value for the kaijo is dependent upon a large number of factors, but it is considered that in the case of silk from *Bombyx mori*, the reactions of an aqueous solution of the sericin are indicative of the kaijo. Thus, the aqueous extract from cocoons of good kaijo has a higher p_H value than that from cocoons of poor kaijo, the gold number of the sericin solution is high if the kaijo is poor and *vice versa*, and the emulsifying properties of the sericin are best when the kaijo is good. If the kaijo is low, the fraction of Sericin A in the extract is approximately 40%, but when the kaijo is high, the sericin A content varies from 75·7% to 79·2%. The reeling of silk is easier when the isoelectric point of the solution lies between p_H 4·25 and 4·4, and is said to be improved by a preliminary treatment of the cocoon in a dilute solution of ammonia followed by dilute sodium hydroxide solution (Scott, Amer. Dyestuff Rep. 1934, **23**, 217).

Soaking.—This process consists in softening and lubricating raw silk by soaking in an oil emulsion preparatory to the operation of throwing (twisting) and subsequent weaving or knitting. The older practice was to soak the fibres overnight at 80–100°F. in an emulsion of neatsfoot oil and soap, afterwards removing the excess liquor by hydroextraction, and drying at a temperature below 100°F. As a result of the development of the sulphonated oils, it is now possible to substitute sulphonated neatsfoot oil for soap, and to use mineral oil with this compound. Further advances include the use of wetting agents such as alkylated naphthalenesulphonic acids, sulphonated abietenes and derivatives of glycol, and the use of sodium salts of sulphonated esters of fatty acids or acid amides, or the sodium salts of fatty alcohol sulphonates, as substitutes for soap or sulphonated oils. It is essential that oil used for this purpose should not be liable to oxidation, and that sulphation should be carefully controlled. A recent patent (U.S.P. 2129904) protects the use of a soaking bath containing the oil as a negatively charged disperse phase, to which is added a discharging agent such as ammonium sulphate, fluosilicates or certain acids, thereby causing the oil to be deposited on the fibre.

Degumming.—Degumming is the technical term for the operation of removing sericin, etc., from the raw silk fibre, thus producing the lustrous fibroin. Whilst it is customary to remove the whole of the gum, in special cases a considerable amount is left on the fibre. Souple silk, for example, is raw silk from which only 8–12% of the gum has been removed, and Écru silk is obtained by treating the raw material in lukewarm water, thereby removing 3–4% of sericin. In the usual methods of degumming, not only is it necessary to remove the whole of the sericin, but also the natural fats, waxes and pigments, and, in certain cases, the oils added to assist processing. The reagent most frequently used for this purpose is a hot soap solution. A soda olive-oil soap is normally employed because of the comparative ease with which it can be washed out of the silk, although certain advantages are claimed for the more expensive potassium and triethanolamine soaps. It has been found that the best results are obtained when the process is carried out between p_H 10·0 and 10·5 (Mosher, Amer. Silk J. 1930, **49**, No. 7, 53; No. 8, 54; No. 9, 59) and at a temperature of 200–210°F. Although the time required for degumming varies with the nature of the silk, treatments of 1 to 2 hours' duration in a boiling soap solution at p_H 10·2 are quite effective. The possibility of degumming in alkaline solutions of cheaper reagents such as caustic soda, sodium carbonate, sodium silicate and sodium phosphate has often been contemplated, but the fibroin thus produced is liable to lack lustre and to retain some of the natural waxes. The use of alkalis, together with sulphonated oils, and of buffered alkaline solutions has also received attention. In addition, enzymes such as trypsin, pepsin and papain, bacterial proteolytic ferments, yeast enzymes, diastase from soy wort and preparations from the digestive organs of fish, are employed, but these are rarely able to effect complete removal of sericin, and it is therefore advisable to give a short preliminary treatment in hot acid or alkaline liquors, or a subsequent mild soap degumming. Enzyme degumming, which is carried out at comparatively low p_H values and at a low temperature, is particularly applicable to the removal of sericin from silk contained in union materials, *e.g.* silk in admixture with cotton or wool. In the case of silk in silk-wool mixtures, where it is inadvisable to use solutions of high p_H values, a method of acid degumming at p_H 1·75–2·5 tends to minimise damage to the wool.

Weighting.—Silk has a great affinity for salts of certain metals, and advantage is taken of this property to increase the weight of silk goods, stannic chloride being the salt most commonly employed for this purpose. The silk to be weighted is subjected to alternate soakings in solutions of stannic chloride and sodium phosphate, and washed after each treatment. When sufficiently weighted by this means, it is treated with a solution of sodium silicate and then washed to remove the excess reagent. Views on the mechanism of the process are many and varied (Heermann, Ristenpart—two series of papers by these authors in Farben-Ztg. 1903–1909; Sisley, Chem.-Ztg. 1911, **621**; Ley, *ibid.* 1912, 1405; Fichter and Müller, Farben-Ztg. 1915, **26**, 253, 274, 289; Scott, Amer. Dyestuff Rep. 1931, **20**, 18, 39, 40, 43, 517, 557, 591, 621), but it would appear that the stannic chloride combines with the silk to form an additive compound which is subsequently hydrolysed on washing with the production of free hydrochloric acid and stannic oxide, which is retained by the silk. Further treatment with sodium phosphate and silicate results in the formation, on the fibre, of a tin silico-phosphate complex of indefinite composition. There are numerous modifications of this procedure, but in general, immersion in some solution of a metallic salt is followed by treatment with a salt which will react to form an insoluble precipitate in or on the fibre. Sodium chloride, calcium acetate and certain carbonates or sulphocyanates may be added to the stannic chloride bath, and ammonium hydrogen phosphate substituted for sodium phosphate. A preliminary treatment of the fibre with formic acid, chloroacetic acid or 26% hydrochloric acid is sometimes advantageous. When lead salts are used for weighting, the silk is subjected to one or two cycles of alternate tin and phosphate treatments, then acidified with dilute acetic acid, and treated with a solution of lead acetate followed by fixation with sodium phosphate. Lead acetate may be replaced by lead chloride if other modifications are also introduced. Basic aluminium nitrate, chromium compounds, antimony chloride, iron salts, ammoniacal zinc acetate, rare-earth metal salts, and various organic substances (*e.g.* gelatine, dextrose, logwood and tannins) are further examples of the many reagents which are employed. Practically all weighting materials have a deleterious effect on silk, and weighted silks deteriorate more rapidly than unweighted (Johnson and Edgar, Iowa State Coll. J. Sci. 1936, **11**, 5). The presence of weighting may often be detected quite simply by igniting the fibre, which, if heavily weighted, will not inflame, but gradually smoulder away, leaving a coherent ash which retains the original form of the fibre. The percentage of true silk in a weighted sample is most accurately determined by estimating the total nitrogen content by the Kjeldahl process, but since the weighting material may also contain nitrogen, for example, gelatin and Prussian blue, this must first be removed by boiling in acid and in alkali. Complete analysis of a sample of weighted silk is complicated by the immense variety of possible weighting agents, and the accuracy is impaired by the uncertainty of the correction to be applied for the loss of silk substance at the different stages. Details of such analyses are given in Allen, " Commercial Organic Analysis," 5th ed. 1933, X, 222.

The final processes in the manufacture of silk. are dyeing and finishing, and many diverse effects, such as modification of transparency, lustre and handle, may result from these operations. The fibres readily adsorb both acid and basic colours. Vat dyes, mordant dyes and logwood blacks are widely used in silk dyeing, and direct and basic colours in printing (*v.* Vol. IV, 144).

Testing.

(*a*) *Determination of Silk in Admixture with other Fibres.*—Qualitatively, silk may be detected by its appearance under the microscope and by positive reactions on application of the usual tests for proteins. It may be distinguished from the wild silks by a greater reactivity, being more soluble in boiling concentrated hydrochloric acid, concentrated potassium hydroxide and ammoniacal copper hydroxide. Quantitative methods of estimating silk in admixture with other fibres are based upon preferential solution of the silk fibres. A reagent made by dissolving 16 g. copper sulphate in 140–160 ml. water, adding 8–10 g. glycerol, and then pouring in sodium hydroxide solution until the precipitate is just redissolved, is capable of dissolving silk entirely, but removes only 1·0–1·5% by weight of cotton and 9–16% by weight of wool. A boiling solution of oxychloride of zinc is another preferential solvent, and Richardson claims that an ammoniacal solution of nickel oxide is also satisfactory. Silk dissolves in the cold in the latter reagent, whilst cotton loses 0·45% of its weight and wool 0·33%, but for analytical purposes, it is recommended that solution should be carried out at the boil. Full details of these tests may be found in Allen, *op. cit.*, p. 217.

(*b*) *The Measurement of Damage.*—The term damage includes modification of the protein by acids, alkalis, oxidising agents, light, steam and dry heat, and it is doubtful whether all the methods which have been devised for its detection and estimation yield comparable results. Measurements of wet and dry tensile strength and elongation have been extensively employed (Johnson and Edgar, *l.c.*), and microscopic observation is a useful qualitative indication. Kaneko (J. Agric. Chem. Soc. Japan, 1937, **13**, 217) has advocated the use of Zimmermann's reagent (a solution of *o*-phthalaldehyde made acid with hydrochloric acid), since this gives no colour with degummed and undamaged silk, but produces a violet coloration with damaged silk or silk gum. Determinations of total nitrogen content and amino-nitrogen content have also been carried out as an indication of damage (Harris, Amer. Dyestuff Rep. 1934, **23**, 403; 1937, **26**, 650), but probably the most satisfactory method involves measurement of the viscosity in zinc chloride solution of specific gravity 1·67. The original method of Trotman and Bell (J.S.C.I. 1935, **54**, 141T), as modified by Tweedie (Canad. J. Res. 1938, **16**, B, 134), consists in placing 2·50 g. of silk (of standard regain) in a flask and adding 100 ml. zinc chloride solution d^{20} 1·67. After dissolving the silk by warming in an oven at 45°C. for 3 hours, the flask is cooled and the viscosity measured at 20°C. Undamaged silk gives viscosities of 19–24 centipoises, but damaged material gives values lower than 19. The viscosity is decreased only when silk has been damaged by chemical means, mechanical damage having no effect (Shinkle, Amer. Dyestuff Rep. 1939, **28**, 374).

General References.—Scott, " Chemistry of Silk and Silk Processing," Amer. Dyestuff Rep. 1934, **23**, 217, 253, 283, 330, 339; 1936, **25**, 451; 1937, **26**, 756; 1938, **27**, 710; 1939, **28**, 501. Denham and Crummett, Survey of Recent Progress, I Textile Fibres—Silk, J. Soc. Dyers and Col. 1925, **41**, 19. Annual Reports for Applied Chemistry, Society of Chemistry and Industry. Matthews, " Textile Fibers," 4th ed., Wiley & Sons, New York, 1924. Trotman, "Bleaching, Dyeing and Chemical Technology of Textile Fibres," Griffin, London, 1925.

C. S. W.

FIBRES, ANIMAL, WOOL AND RELATED FIBRES. *Mode of Growth.*—Animal fibres, such as wool and hair, grow from the base of a follicle or tube-like depression in the skin, as shown in Fig. 1 (Duerden, J. Text. Inst. 1926, **17**, T268). That part of the fibre which projects beyond the surface of the skin is known as the shaft, and the portion embedded in the skin is called the root. At its lower end, the root expands into a bulb, into which projects the papilla, formed from the dermis. Growth of the fibre takes place by the formation of cells at the base of the follicle, in the neighbourhood of the papilla, the fibre being extruded as more cells develop below. The contents of the cells are at first fluid, but changes occur during their passage up the root sheath. Such changes result in a hardening or keratinisation of the structure, and the cross-sectional area of the fibre diminishes progressively as shown in Fig. 1.

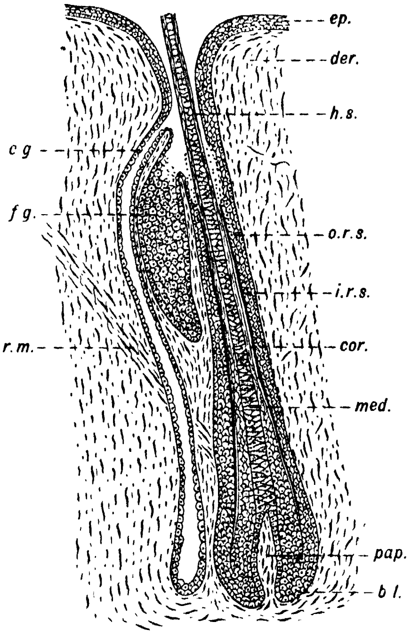


FIG. 1.

a.r.m., arrector pili muscle.
b.l., basal layer.
c.g., coil gland.
cor., cortex of fibre.
der., dermis of skin.
ep., epidermis of skin.
f.g., fat gland.
h.s., hair shaft.
i.r.s., inner root sheath.
med., medulla.
o.r.s., outer root sheath.
pap., papilla.

As it emerges from the skin, each fibre is coated with a layer of fat derived from the sebaceous gland, which opens on to the fibre near the surface of the skin. In addition, the fibres are contaminated with suint from the sudoriferous or coil glands. The latter may emerge alongside the fibre, as shown in Fig. 1, or at the surface of the skin away from the fibre. In its raw state, therefore, wool is contaminated with wool fat and suint, the former containing esters of cholesterol, and the latter potassium salts of organic acids. Since both suint and wool are hygroscopic, the greasy wool contains water, as well as dirt and vegetable matter.

Greasy wool may be readily analysed by Wilson's procedure (J. Text. Science, 1926, 99; 1927, 10). A known weight is extracted first with ether to remove wool fat, and then with water to remove suint. Coarse mineral matter may then be removed from the residual wool by teasing it out under water. The mineral matter settles to the bottom of the vessel and may be collected, dried and weighed. After being allowed to dry in the air, the washed wool can be freed from vegetable matter by means of forceps, and the dry weight of clean wool estimated, either by drying in a stream of dry air at 105°C., or by exposure to phosphorus pentoxide *in vacuo.*

Typical analyses of greasy wool are given in Table I (Veitch and Benedict, Trans. Amer. Inst. Chem. Eng., 1924, **16**, Pt. 2, 259).

TABLE I.

Wool quality.	No. of samples.	Moisture.	Wool fat.	Suint.
		%	%	%
Fines . .	93	5·6	17·4	14·0
½ blood .	48	5·5	12·7	15·2
Medium .	29	5·0	10·5	14·7
⅜ blood .	44	6·3	9·8	16·8
¼ blood .	38	7·0	8·6	15·4

On the average, therefore, the fat content of greasy wool increases with the quality (fineness) of the fibres, but the suint content is sensibly independent of wool quality.

Dimensional Characteristics.—Wool fibres vary considerably in length, fineness and crimpiness, not merely from one type of wool to another, but even within a single staple. The average fibre-length of Shropshire wool, for example, is only 2·5 in., whereas that of Wensleydale wool is 12·7 in. In the case of Shropshire wool, the variation in length is from 1·75 to 3·25 in., and in the case of Wensleydale wool from 6·5 to 16·0 in. (Barker, J. Text. Science, 1924, 1st Special Issue, 33). There is no simple relationship between fibre-length and wool quality, as estimated by the grower, but the fineness of the fibres, and the number of waves or crimps per inch, increase with increasing wool quality, as is indicated by the data for Merino wools given in Table II (Duerden, J. Text. Inst. 1929, **20**, T93).

The origin of crimpiness in wool is as yet unknown, but a highly significant observation was made in 1928 by Lefroy of Walebing, West Australia (quoted by Barker and Norris, *ibid.* 1930, **21**, T1). He noticed that in a certain lock of wool, which had been allowed to grow for twelve months, the *number* of crimps produced in each successive period of 4 months was constant, but the length of wool produced in the various periods, and therefore the size of the crimps, was distinctly variable. This observa-

TABLE II.

Quality Number.	Thickness limits. μ	Crimps per in.
Above 120's	14·0–14·7	28–30 ; 27–30
120's	14·7–15·4	25–27 ; 24–27
100's	15·4–16·2	22–24 ; 21–24
90's	16·2–17·0	20–21 ; 19–21
80's	17·0–17·9	18–19 ; 17–19
70's	17·9–18·9	16–17 ; 15–17
66's	18·9–20·0	14–15 ; 13–15
64's	20·0–21·3	12–13 ; 11–13
60's	21·3–23·0	10–11 ; 9–11
58's	23·0–25·5	8–9 ; 7–9
56's	25·5–29·0	6–7 ; 5–7

tion that crimp is a periodic function of time was afterwards confirmed by Norris and Rensburg (*ibid.* 1930, **21**, T481), who determined the number of crimps in fibres of varying length taken from a single staple. Typical results are given in Table III for a 60's–64's Cape Merino wool.

TABLE III.

Length group (cms.).	Mean number of crimps.	
	Per fibre.	Per cm.
9 –10	45	4·74
10·1–11	43	4·10
11·1–12	43	3·75
12·1–13	45	3·60
13·1–14	45	3·33
14·1–15	45	3·10
15·1–16	46	2·97

Microscopic Appearance.—Under the microscope, animal fibres are seen to be covered by a layer of overlapping scales, which appear to vary in size and shape as shown in Fig. 2 (Manby, J. Roy. Microscop. Soc. 1933, **53**, 9). According to Nathusius, however, the size and nature of the cells of the cuticle are the same for various types of wool, the different appearances of different types of fibre being due to variations in the rate of growth relative to the number of scales formed, and, therefore, in the extent to which each scale overlaps another. Such variations are clearly indicated by the data of Table IV (Hoffmann, Jahrb. Landw. 1925, **61**, Pt. 5).

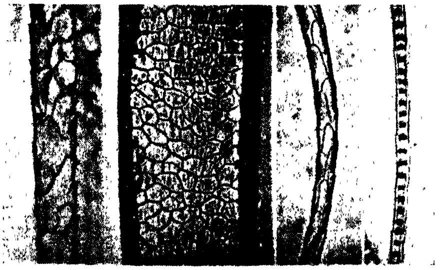


FIG. 2.

a Leicester wool.
b Moufion wool.
c, *d* *Ornithorynchus anatinus* fur hair.

TABLE IV.

Wool.	No. of scales per 1,000,000μ^2 surface.
Leicester	1,510
Southdown	2,090
Eskurial	2,637
French Merino	2,654
Rhön	2,948
Hampshire	3,623

According to Hoffmann (*l.c.*) the surface area occupied by each scale is characteristic of the breed of sheep.

Apart from the surface scale structure, little else is to be seen under the microscope, except in the case of hairs and coarse wools, which may show dark islands or continuous bands, patterned in various ways, along the fibre axis. Such islands or bands constitute the medulla, which consists of hollow cells. The appearance of a number of medullated fibres, photographed by transmitted light, is shown in Fig. 3, the dark appearance of the medulla being due, of course, to scattering of light by the hollow cells. True wool contains no medulla, which is characteristic of the hairs, but since the covering of the primi-

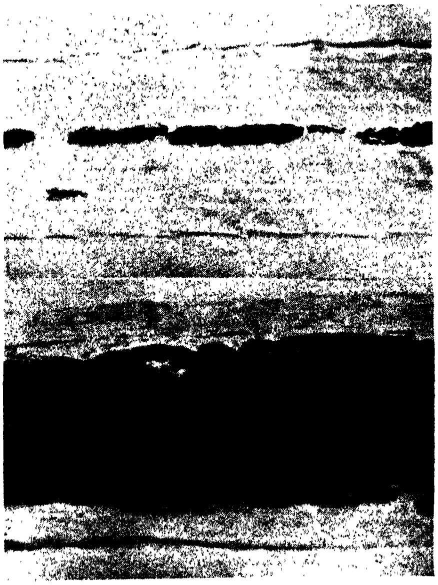


FIG. 3.—MEDULLATED WOOL FIBRES.

tive sheep consisted of two coats—an outer coat of hair and an under coat of wool—there is always a tendency for medullated fibres to reappear in the fleece. This tendency is naturally most pronounced in the Mountain breeds of sheep, which are exposed to severe climatic conditions, and their fleeces contain a large proportion of highly medullated fibres, known as *kemps*. The hollow character of medullary cells is well illustrated by the photomicrograph of a cross-section of a kempy fibre in Fig. 4. When a kempy wool is dyed, the kemps in certain cases seem to remain uncoloured, but the effect is an optical illusion because a higher proportion of white light is reflected by the hollow cells.

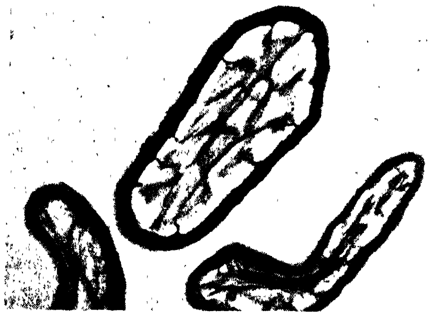


Fig. 4.—Cross-Sections of Kemp Fibres.

Between the cuticle and the medulla of hairs and medullated fibres, and within the cuticle of non-medullated fibres, is the cortex. This consists of cortical cells which are not to be distinguished under the microscope but may be isolated in various ways. Nathusius revealed their presence by treating wool with dilute ammonia at a low temperature for many days: when pressure was applied to the treated fibres, they disintegrated into their constituent cells. Waters (New Zealand J. Agric. 1923, **1**, 35) showed that a bacterium isolated from "pink rotted" wool is capable of disintegrating sound wool under artificial conditions. Use was made of the bacterium by Gabriel (J. Text. Inst. 1932, **23**, T171) to isolate the cortical cells of Merino, Romney and Lincoln wools. On examination, the cells were found to vary in length from about 70 to 150μ in each case, but the average length (400–500 observations) seemed to be independent of wool quality. The values obtained were 106·9, 108 and 114μ for the Merino, Romney and Lincoln wools, respectively. Finally, Burgess (*ibid.* 1934, **25**, T289) showed that a 0·25% solution of trypsin at p_H 8·6 will disintegrate wool in about 2 days at 35–40°C. The main interest of these methods is that they allow the cortical cells, which are not visible under the microscope, to be isolated and examined, but the cuticular scales are, of course, isolated at the same time.

Chemical Composition.

Elementary Analysis.—Bowman, "Structure of the Wool Fibre," MacMillan & Co., Ltd., 1908, p. 244, analysed four wools and obtained the data given in Table V.

Table V.

Element.	Lincoln. wool.	Irish wool.	Northumberland wool.	Southdown wool.
Carbon .	52·0	49·8	50·8	51·3
Hydrogen .	6·9	7·2	7·2	6·9
Nitrogen .	18·1	19·1	18·5	17·8
Oxygen .	20·3	19·9	21·2	20·2
Sulphur .	2·5	3·0	2·3	3·8
Loss . .	0·2	1·0	—	—

Too great reliance should not be placed on the data, however, because the wools were soap-scoured, and it was not then known that adsorbed soap is retained by wool, even after prolonged washing in running water.

More reliable data for the nitrogen and sulphur contents of animal fibres have since been obtained by other observers using raw wool which had been purified by extraction with benzene at a low temperature, followed by washing in water. Some of Barritt's results (J.S.C.I. 1928, **47**, 69T) for the nitrogen content of different fibres are given in Table VI.

Table VI.

Fibre	Nitrogen Content (% on dry weight).
Alpaca (black)	15·85
Alpaca (brown)	16·66
Alpaca (white)	17·00
Dog wool	16·44
Rabbit wool	16·72
Mohair (fine)	16·83
Mohair (coarse)	16·70
Lincoln wool (white) . . .	16·80
Lincoln wool (yellow) . .	16·62
Australian Merino lamb . .	16·73
Monte Video wool . . .	17·07

The nitrogen content of animal fibres, even the nitrogen content of different wools, is distinctly variable. More definite evidence of the variable composition of animal fibres is afforded by the results of sulphur determinations.

Originally, Trotman and Bell (*ibid.* 1926, **45**, 10T) claimed that the sulphur content of different wools was practically constant, the maximum value being 3·42% and the mean of 40 experiments 3·22%. Two years later, Marston (Bulletin No. 38, 1928, Commonwealth of Australia Council for Scientific and Industrial Research) lent support to this view, but he found the sulphur content of Australian wools to lie outside Trotman's range, between 3·59 and 3·52%. In the meantime, however, Barritt and King (J. Text. Inst. 1926, **17**, T386) had shown the sulphur content of both wool and mohair to be decidedly variable. Because of the discrepancy, Barritt and King re-examined the question (*ibid.* 1929, **20**, T151) and their results for 64 types of fibre leave no doubt that the sulphur content of animal fibres is definitely variable. Selected data are given in Table VII.

TABLE VII.

Fibre.	Sulphur content (% on dry weight).
Alpaca (black)	3·90
Alpaca (brown)	4·35
Alpaca (white)	3·93
Dog wool	5·07
Rabbit wool (agouti)	4·30
Rabbit wool (black).	4·14
Turkey Mohair (fine)	3·36
Turkey Mohair (coarse medullated)	3·03
English Lincoln wool A. . . .	3·10
English Lincoln wool B. . . .	3·26
Australian Merino wool (ram) . .	3·88
,, ,, ,, (ewe) . .	3·91
,, ,, ,, (ewe) . .	3·46
Welsh Mountain wool P5 . . .	4·00
,, ,, ,, P65 . . .	4·13
,, ,, ,, S10 . . .	3·75
Scotch Blackface (fine)	3·82
,, ,, (medullated). .	3·33
,, ,, (kemps) . . .	3·24

Not only does the sulphur content of different types of fibre vary, but even the sulphur content of different wools may vary by as much as 25% (from 3·10 for English Lincoln wool to 4·13 for Welsh Mountain wool).

Wool contains about 0·5% of methionine (Barritt, Nature, 1933, **131**, 689), but apart from this the whole of the sulphur present can be accounted for as cystine (Rimington, Biochem. J. 1929, **23**, 41). Thus the above variations in the sulphur content of animal fibres imply corresponding variations in cystine content. Although the composition of wool depends to a considerable extent on its origin, it might be assumed that the properties of the fibre could be studied by restricting attention to one kind of wool in order to eliminate variations in composition. Unfortunately wool fibres vary in composition along their length, as is indicated by Bonsma's data (J. Text. Inst. 1931, **22**, T305) for the sulphur content of tip, middle and root sections of single staples taken from veld-grown Cape Merino fleeces (Table VIII).

TABLE VIII.

Fraction.	Sulphur Content (% on dry weight).
Tip	3·66
Middle	3·63
Root.	3·81
Tip	3·54
Middle	3·38
Root.	3·71
Tip	3·62
Middle	3·44
Root.	3·71

Such variations in composition along the length of the staple were shown to be related to the nutritional value of the pasture at the time each section was grown: the higher the nutritional value, the higher the sulphur content.

Variation in composition along the length of the staple may also result from the action of light and air on the tip section, which is inevitably exposed to light during growth. The existence of damage of this kind was recognised by von Bergen (Textilber. 1923, **4**, 23; 1925, **6**, 745; 1926, **7**, 451), but its extent is best illustrated by data (Table IX) for the sulphur contents of tip, middle and root sections of New Zealand Romney wool (McMahon and Speakman, Trans. Faraday Soc. 1937, **33**, 844). The staples were taken from a single animal, part of whose fleece had been fitted with a fabric cover. Whereas the britch and neck wools were freely exposed to light during the whole period of growth, that from the side was protected by the cover.

TABLE IX.

Section	Sulphur Content (% on dry weight) of :		
	Britch (exposed).	Neck (exposed).	Side (covered).
Tip. . .	2·78	2·83	3·27
Middle. .	3·26	3·18	3·23
Root . .	3·45	3·55	3·53

Thus about 14% of the total sulphur in the tip wool is lost when the fibres are exposed to light during growth. The loss was shown to be due to attack on the cystine bond as follows:

$$\mathrm{RCH_2{\cdot}S{\cdot}S{\cdot}CH_2R + H_2O}$$
$$\mathrm{RCH_2SH + RCH_2S{\cdot}OH.}$$
$$\mathrm{RCH_2S{\cdot}OH \rightarrow RCHO + H_2S.}$$

Ultimately, the hydrogen sulphide is, of course, converted to sulphur dioxide and sulphuric acid.

For experimental work on intact wool fibres, therefore, only the root ends must be used. Even if such wool were grown under carefully controlled conditions, however, its composition would still be variable, because the different types of cell in the fibre differ in constitution. Reference to the data for Scotch Blackface wool in Table VII shows that, as the degree of medullation of a fibre increases, the sulphur content decreases. This observation led Barritt and King (*l.c.*) to suggest that the medullary cells are either free from or deficient in sulphur. Jordan Lloyd and Marriott (Biochem. J. 1933, **27**, 911) have substantiated this deduction in the case of goat hair. They discovered that the cuticle and cortex of animal hairs are dissolved by 4*N*-caustic soda solution, whereas the medulla remains undissolved and apparently intact. The sulphur content of the latter was found to be 0·23%, whilst that of the cortex and cuticle was 3·60%. King and Nichols (Trans. Faraday Soc. 1933, **29**, 272), from consideration of the shape of the follicle and the accessibility of its various parts to the blood stream, have since argued that there should be a sulphur gradient from the outside of the fibre to the interior, the cuticle containing the most, and the axis the least, sulphur. No evidence was advanced in support of the hypothesis, which seems to be untrue because Chamberlain (J. Text. Inst. 1932, **23**, T13) showed that when human hair, having a sulphur content of 5·02%, was descaled until it had lost as much as 15·3% by weight, the sulphur content of the residual descaled hair remained unchanged at 5·02%. The fibres were, of course, non-medullated.

Although the scales and cortex do not, therefore, differ as regards sulphur content, cystine is not distributed uniformly over the cross-section of a non-medullated fibre. Stakheyewa-Kaverznewa and Gavrilow (Bull. Soc. chim. (Mémoires), 1937, **4**, 647) have, for example, shown that the cells isolated from wool by means of pancreatin possess a sulphur content of 3·05% compared with 2·91% for the original wool. Similarly, Speakman and McMahon (Nature, 1938, **141**, 118) found that the sulphur content of the cells, isolated from an Australian merino wool by means of trypsin, increased with increasing time of retting from 3·61% after 14 days to 3·87% after 30 days, the sulphur content of the original wool (intact root ends) being 3·51%. The intercellular phase which is removed in both sets of experiments is clearly deficient in sulphur.

Finally, even though scales and cortex have the same sulphur content, they do differ in composition, as may be shown by means of the Pauly test for histidine and tyrosine (Mark, "Beiträge zur Kenntnis der Wolle und ihrer Bearbeitung," 1925, p. 41; Burgess, J. Text. Inst. 1929, **19**, T315; Rimington, *ibid.* 1930, **21**, T237). Both these amino-acids give a reddish-brown coloration with diazobenzenesulphonic acid, but, although they are known to be present in wool, intact fibres give no colour with the reagent, except at the cut ends. In the case of chemically or mechanically damaged fibres, a coloration is obtained wherever the cortex is exposed, but the cuticle itself remains unstained. Hence the cortex of animal fibres contains tyrosine and/or histidine, whereas the cuticle appears to contain neither.

From this brief survey of analytical work on animal fibres, it is evident that they show bewildering variation in composition. By the methods described below it has, however, been possible to elucidate a skeleton structure— a highest common factor of structure—which is capable of ready adaptation to include the variations in the composition of animal fibres.

Amino-Acid Analysis.—The argument commences with the fact that when animal fibres like wool are boiled with 20% hydrochloric acid solution for several hours, they are broken down into the constituent amino-acids, which have the general formula: $NH_2{\cdot}CH(R){\cdot}COOH$. The radical *R* may be inert, *e.g.* glycine; basic, *e.g.* arginine; or acidic, *e.g.* glutamic acid. By suitable chemical methods, the various amino-acids present in the hydrolysate may be separated, isolated and estimated (Lloyd and Shore, "Chemistry of the Proteins," Churchill, 1938, p. 101). The results obtained by various observers with wool are summarised in Table X.

TABLE X.

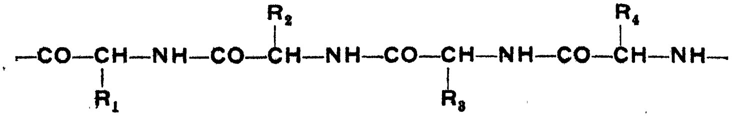
Substance.	Amount (g.) isolated from 100 g. dry wool.
Glycine . .	0·6 (A & V).
Alanine . .	4·4 (A & V).
Valine . .	2·8 (A & V).
Leucine . .	11·5 (A & V).
Serine. . .	2·9 (A & V).
Proline . .	4·4 (A & V).
Cystine . .	13·1 (M), 15·5 (calc.).
Aspartic acid.	2·3 (A & V); 7·27 (S & T).
Glutamic acid	12·9 (A & V); 15·27 (S & T).
Arginine . .	10·2 (M); 7·8 (V & B); 8·0 (V & L) human hair.
Lysine . .	2·8 (M); 2·3 (V & B); 2·5 (V & L) human hair.
Histidine . .	6·9 (M); 0·7 (V & B); 0·9 (V & L) human hair.
Tyrosine . .	4·8 (M).
Tryptophane.	1·8 (M).
Amide nitrogen	1·2 (M); 1·37 (S & T).

References: Abderhalden and Voitinovici, Z. physiol. Chem.; 1907, **52**, 368: Marston (*l.c.*); Vickery and Block, J. Biol. Chem. 1930, **86**, 107; Vickery and Leavenworth, *ibid.* 1929, **83**, 523; Speakman and Townend, Nature, 1937, **139**, 411.

Note: The second, calculated, value for cystine is derived from the sulphur content of Welsh Mountain wool, p. 99, Table VII, on the assumption that the whole of the sulphur is present as cystine.

Vickery and Block's data for the basic amino-acids in wool were obtained by isolating the acids from the hydrolysate, and the results are probably low, especially as they fail to account for the acid-combining capacity of wool. Marston's values for the arginine and lysine content of wool were obtained by indirect methods and are probably more reliable, but his value for the histidine content is incorrect. Finally, Abderhalden and Voitinovici's determinations of the dicarboxylic acids are low because they were made before improved methods of estimation had been evolved. Selecting the more reliable data, wherever a choice is possible, the results of Table X indicate that from 100 g. dry wool, 85 g. amino-acids have been isolated and identified. The analysis is, however, less complete than such a statement would indicate, because the fibre is formed from the amino-acids with elimination of water, as indicated below.

In agreement with Fischer's views, the results of X-ray and chemical studies of the structure of the wool fibre indicate that the latter consists of long polypeptide chains, which are formed by the condensation of the amino-acids through α-amino- and their associated carboxyl groups as follows:



$$—CO—\underset{R_1}{\underset{|}{CH}}—NH—CO—\overset{R_2}{\overset{|}{CH}}—NH—CO—\underset{R_3}{\underset{|}{CH}}—NH—CO—\overset{R_4}{\overset{|}{CH}}—NH—$$

where R_1, R_2, R_3, R_4 represent the side chains characteristic of the various amino-acids in the chain. The long molecules are arranged approximately parallel to one another and to the length of the fibre, and it is now generally recognised that the peptide chains are linked together in one plane by cystine and salt linkages as shown in Fig. 5.

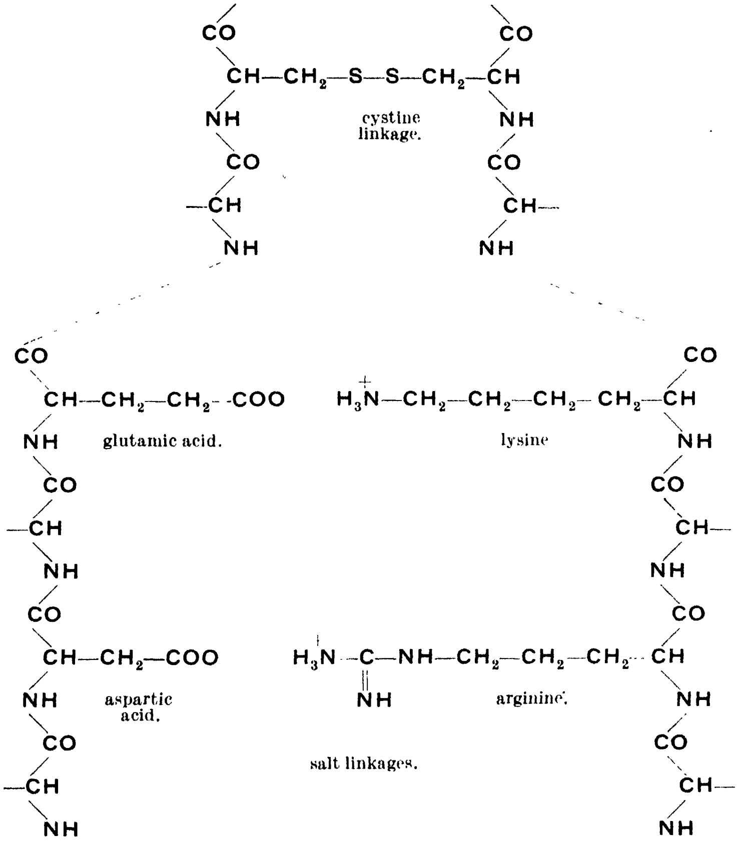


Fig. 5.

The analytical data of Table X indicate that the acid and basic side-chains of wool are equivalent: the aspartic and glutamic acids present in wool are equivalent to 22·10 mg.N/g. wool. After deducting amide nitrogen (13·7 mg./g.), the excess of free acid side-chains is equivalent to 8·4 mg.N/g. For combination with the amounts of arginine, lysine and histidine isolated by Vickery and Block, dicarboxylic acid equivalent to 8·55 mg.N/g. would be required. Even if the maximum combining capacity of wool for hydrochloric acid is taken as a measure of the basic amino-acid content, the amount of dicarboxylic acid needed for combination is only 11·2 mg.N/g. Expressed in another way, the amide nitrogen and basic amino-acids present in wool demand a dicarboxylic acid content of 24·9 mg.N/g., as compared with the isolated amount of 22·19 mg.N/g., if the *free* acid and basic side-chains are equivalent. Such close agreement is sufficient to establish the equivalence which was originally postulated in order to explain the elastic properties of animal fibres in media of varying p_H (Speakman and Hirst, Trans. Faraday Soc. 1933, **29**, 148). The fact that the free acid and basic side-chains are combined to form salt linkages as shown in Fig. 5 was deduced from the preceding investigation, and confirmed by determinations of the titration curve of wool (Speakman and Stott, *ibid.* 1934, **30**, 539), and by examining the elastic properties of de-aminated fibres in media of varying p_H (*idem*, Nature, 1938, **141**, 414).

That the polypeptide chains in wool are bridged by cystine linkages as well as salt linkages seems probable from first principles, and is supported by the resistance of the fibre to swelling and solution in acids. As shown in Fig. 6, the increase in diameter of Cotswold wool fibres on transference from water to hydrochloric or sulphuric acid solution at p_H 1, is only about 3%, in striking contrast with the behaviour of proteins such as gelatin, from which cystine is absent (Speakman and Stott, *l.c.*). Further, wool passes into solution readily when treated with sodium sulphide solution, which is capable of breaking the disulphide bond. Similarly, when wool is treated with chlorine peroxide, which is known to oxidise cystine to cysteic acid, the product is capable of solution in such solvents as are normally employed to dissolve silk. These and a number of other observations which are given below, have been used to establish the fact that the polypeptide chains of animal fibres such as wool are bridged by cystine linkages as shown in Fig. 5. The figure may be regarded as a skeleton structure of the wool molecule, and it is obviously capable of adaptation to take account of variations in composition of the fibre: variations in sulphur content imply variations in the number of cystine linkages, but the structure remains unaltered in its essentials, no matter how great such variations may be.

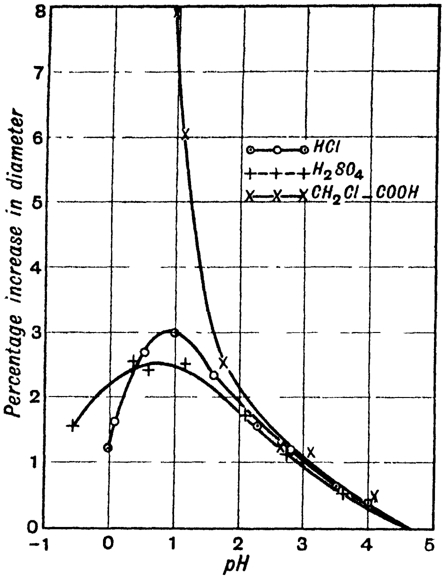
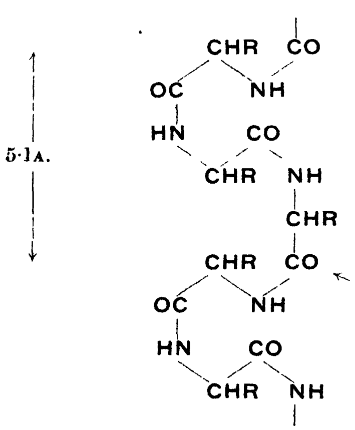


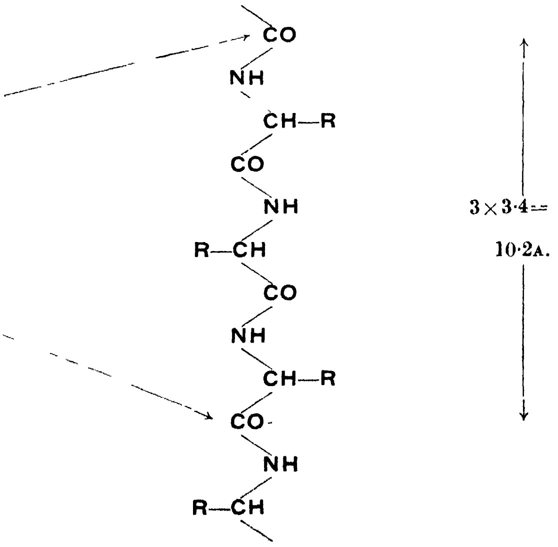
FIG. 6.—SWELLING OF WOOL FIBRES IN ACIDS.

As shown in Fig. 5, the distance apart of the main peptide chains in the plane of the cross-linkages must vary in order to accommodate cross-linkages of varying length. In addition, however, it has been established by combining the results of X-ray analysis (Astbury and Street, Phil. Trans. 1931, A, **230**, 75; Astbury and Woods, *ibid.* 1933, A, **232**, 333) with studies of the elastic properties of wool fibres in water under various conditions (Shorter, J. Text. Inst. 1924, **15**, T207; Speakman, *ibid.* 1926, **17**, T457; Proc. Roy. Soc. 1928, B, **103**, 377; Trans. Faraday Soc. 1929, **25**, 92; Proc. Roy. Soc. 1931, A, **132**, 167; Astbury and Woods, *l.c.*) that the main peptide chains of unstretched wool fibres are folded at right angles to the plane of the cross-linkages as shown in Fig. 7.



α keratin.

FIG. 7.

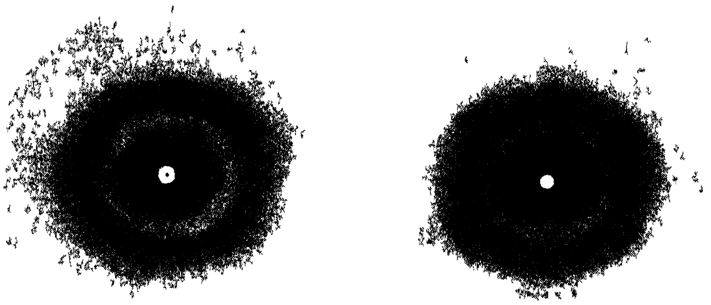


β-keratin.

FIG. 8.

When the fibre is stretched, the folded structure, known as α-keratin, unfolds to give β-keratin, shown in Fig. 8. Typical X-ray photographs (Astbury) of stretched and unstretched wool fibres are given in Fig. 9.

Both physico-chemical (Speakman, Proc. Roy. Soc. 1931, A, **132**, 167; Trans. Faraday Soc. 1933, **29**, 148; J. Soc. Dyers and Col., Jubilee Number, 1934, p. 43) and X-ray (Astbury and Sisson, Proc. Roy. Soc. 1935, A, **150**, 533), investigations agree in indicating that the long, folded peptide chains are linked together *in one plane* by cystine and salt linkages, several such planes being superimposed to form the crystals of the fibre. The size of these crystals has also been deduced by physico-chemical methods (Speakman, *ibid* 1931, A, **132**, 167) their thickness is not more than 200 A, their length is about 10 times the thickness and they are lamellar in shape According to X-ray observations, the *average* thickness of the crystals is about 100 A (Astbury, *l c*) in close agreement with the value obtained by indirect physico-chemical methods



α keratin β keratin

Fig 9

PHYSICAL PROPERTIES

(*a*) *Water Adsorption* —The cohesion of animal fibres is clearly due to cystine linkages, salt linkages and the attractive force between —**CO**— and —**NH**— groups (Figs 5 and 7) At ordinary temperatures, therefore, the cohesion of wool will be reduced by water adsorption because the attraction between the oppositely charged ions of salt linkages, and between —**CO**— and —**NH**— groups, is reduced in presence of water This effect is accentuated by rise of temperature, not merely because of increased thermal agitation, but also because the cystine linkages are attacked by hot water, especially if the fibre is in a state of strain Before discussing the elastic properties of animal fibres, however, it is clearly essential to possess water adsorption data

TABLE XI

Relative humidity (%)	Water adsorbed (% on dry weight)
	Adsorption
7 0	3 40
25 0	6 96
34 2	8 41
49 8	11 22
63 3	13 97
75 0	16 69
92 5	23 81
100 0	33 3
	Desorption
92 5	24 70
75 0	18 69
63 3	16 12
48 7	13 36
34 2	10 57
7 0	4 77

The amount of water adsorbed by six wools at 25° C has been studied as a function of the relative humidity of the atmosphere by Speakman (J S C I 1930, **49**, 209T) Data for a Geelong 80's merino wool are given in Table XI The extent of hysteresis between adsorption and desorption is considerable, and in a later paper, Speakman and Cooper ((J Text Inst 1936, **27**, T183) showed that the range of humidity over which wool must be dried in order to pass from adsorption to limiting desorption conditions is independent of regain and is about 18% Since wool adsorbs water with evolution of heat (Hedges, Trans Faraday Soc 1926, **22**, 178), the amount of water adsorbed should decrease with rise of temperature at constant relative humidity. Although confirming this deduction, early determinations of the influence of temperature on water adsorption (Schloesing, Rapports de la Société d'Encouragement pour l'Industrie Nationale, Paris, 1893, Hedges, *l.c.*) took no account of adsorption hysteresis, and Goodings' more recent determinations (Amer. Dyestuff Rep. 1935, **24**, 109) relate to only two temperatures, 10° and 30°C. More extensive observations have since been made by Speakman and Cooper (J Text Inst 1936, **27**, T183) who showed that the amount of water adsorbed by wool decreases as a linear function of temperature when the partial pressure of water vapour is low When the partial pressure is 0 975, however, the isobar shows a minimum at about 43°C, confirming the view (Speakman, Stott and Chang, *ibid* 1933, **24**, T273) that the swelling of wool in water is at a minimum in the neighbourhood of 40°C The adsorption isotherms were determined with English Leicester wool at intervals of 5°C from 25° to 55°C, but complete isotherms could not be obtained above 55°C because the disulphide bond of wool is attacked and hydrolysed by water vapour at high temperatures, volatile sulphur compounds being evolved Although the temperature and relative humidity of the atmosphere are the main factors influencing the adsorption of water by wool, Speakman and Stott (*ibid.* 1936, **27**, T186) have shown that when wool is dried from regains below saturation, its adsorptive power decreases with increasing temperature of drying. The reduction is caused by partial as well as complete drying, but not by drying from saturation, or by heating wool dried at a low temperature. A normal affinity for water may be restored to wool, which has been dried at a high temperature, by allowing it to reach saturation with water vapour, but the reduced adsorptive power of wool which has been heated over water at a high temperature is irreversible.

(*b*) *Elastic Properties.*—In accordance with the preceding argument and observations, the resistance of wool fibres to extension decreases with increasing relative humidity. Typical load-extension curves for Cotswold wool fibres at 25°C. are given in Fig. 10 (Speakman, *ibid.* 1927, **18**, T431), and the manner in which the breaking load and Young's modulus decrease with increasing relative humidity at 22·2°C. is illustrated by the data of Table XII (Speakman, J.S.C.I. 1930, **49**, 209T).

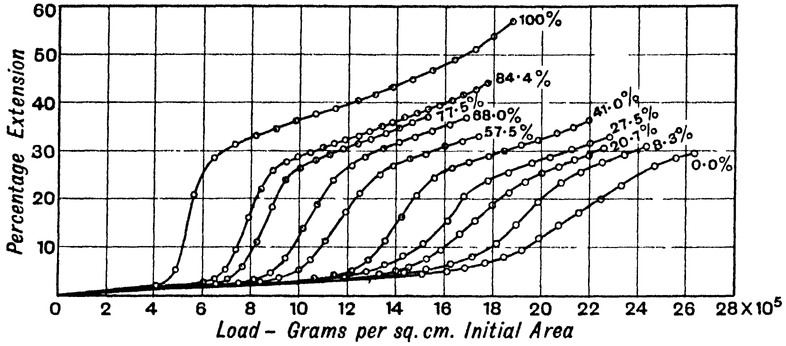


FIG. 10.

TABLE XII.

Relative humidity (%).	Breaking load (g./cm.^{2} initial area).	Young's modulus (dynes cm.^{2}).
0·0	22·1 × 10^5	4·76 × 10^{10}
8·3	21·6 ,,	4·80 ,,
34·2	19·4 ,,	4·19 ,,
49·8	16·8 ,,	3·84 ,,
65·0	16·1 ,,	3·55 ,,
75·0	15·4 ,,	3·28 ,,
100·0	14·9 ,,	1·81 ,,

Even more sensitive to changes of relative humidity than breaking load is the torsional rigidity of wool fibres. Values for the relative rigidity, *i.e.* the rigidity compared with that of a dry fibre, of Cotswold wool fibres at different relative humidities under adsorption and desorption conditions at 25°C. are given in Table XIII

TABLE XIII.

Relative humidity (%):	0·0	10·0	25·0	34·7	49 5	64·5	74·5	89·7	100
Relative rigidity (adsorption):	1·000	0·974	0·920	0·852	0·732	0·584	0·459	0·204	0·068
Relative rigidity (desorption):	1·000	0·982	0·881	0·799	0·679	0·531	0·418	0·192	0·069

(Speakman, Trans. Faraday Soc. 1929, **25**, 92). When plotted against the amount of water adsorbed, adsorption and desorption data lie on a common curve, which has three distinct sections. The intermediate section, covering a range of humidity from 23 to 87%, is linear and is expressed by the equation:

Relative Rigidity = 1·255 - 0·047A,

where A is the amount of water adsorbed.

At constant relative humidity, the resistance of wool fibres to extension decreases with rise of temperature, as is shown by the load-extension curves of Fig. 11 (Speakman, J. Text. Inst. 1927, **18**, T431) for Cotswold wool fibres in water.

Besides being dependent on the temperature and relative humidity of the atmosphere, the elastic properties of animal fibres vary with the rate of loading. This may be illustrated in the first instance by the following data for the extension at break and breaking load of Cotswold wool fibres in water at 18°C. under different rates of loading (Speakman, *l.c.*).

TABLE XIV.—FIBRE DIAMETER = 39μ.

Rate of loading.	Extension at break (%).	Breaking load (g./cm.^{2} initial area).
1 g. every 2 days.	70·2	8·88 × 10^5
1·44 g./min.	48·4	17·1 ,,
3·16 ,,	50·9	18·7 ,,
4·90 ,,	50·4	18·7 ,,
10·72 ,,	50·9	19·3 ,,
15·55 ,,	54·0	20·6 ,,
29·6 ,,	54·3	20·1 ,,
37·4 ,,	54·4	21·0 ,,
70·0 ,,	53·9	21·7 ,,

For finite rates of loading, both the extension at break and the breaking load increase with increasing rates of loading, but the rule breaks down when the rate of loading is extremely small (1 g. every 2 days). When extension in water is rapid, fibres may be stretched about 30%—27·0% for human hair, 34·5% for Cotswold wool—without significant change of properties, *i.e.* if the fibre is stretched twice in succession with a rest of 24 hours between the two extensions, the two load-extension curves are almost identical. This observation (Speakman, *l.c.*) has been turned to considerable advantage in recent studies of the properties of the wool fibre. By utilising calibrated fibres, *i.e.* fibres whose load-extension curves have been determined up to 30% extension, the influence of various reagents and processes may be determined without resorting to the statistical treatment of results obtained with a large number of fibres.

If, however, the fibre is stretched slowly, or is held stretched for any length of time, it undergoes permanent weakening at any extension, especially when the humidity is high. The extent of the weakening, and the manner in which it increases with increasing time of strain, are well illustrated by the data of Table XV, which were obtained as follows (Speakman, Proc. Roy. Soc. 1928, B, **103**, 377): after determining the load-extension curve by rapid extension in water up to 30%, each fibre was allowed to remain at this extension for a certain time before release. The load-extension curve was then redetermined in water at 25°C., this being possible because wool fibres possess perfect elasticity of form in water at ordinary temperatures. From the two load-extension curves for each fibre, the percentage reduction in the work required for a 30% extension, due to relaxation at this extension, was calculated.

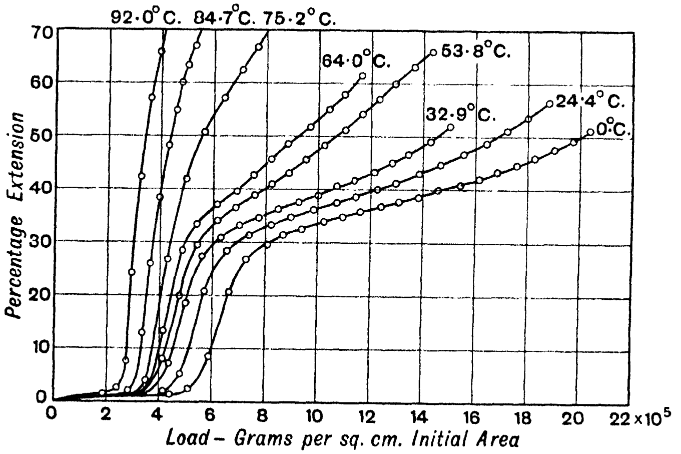


FIG. 11.

TABLE XV.

Time held stretched (Minutes).	Percentage reduction in work for 30% extension.
30	6·5
62	8·5
92	11·5
161	19·2
210	21·5
240	24·4
240	24·6
300	26·7
1,143	40·3

A further illustration of the plasticity of wool is afforded by the following data (Speakman, *l.c.*) for the rate of decay of tension in a fibre at 29% extension in water at 25°C.

Time (minutes).	Tension (g./cm.²).
1·05	$6{\cdot}05 \times 10^5$
1·75	5·89 ,,
2·90	5·74 ,,
4·95	5·58 ,,
7·80	5·42 ,,
11·50	5·26 ,,
16·60	5·11 ,,
22·55	4·95 ,,
30·25	4·80 ,,
39·20	4·64 ,,
50·35	4·49 ,,
62·15	4·33 ,,
76·60	4·17 ,,
1,143	1·97 ,,

The plasticity of wool, as exemplified by the rapid decay of tension in strained fibres, seems to be associated with disulphide bond hydrolysis, because in acid media, where the bond is stable, the rate of decay of tension is small, whereas in alkaline media, where the bond is readily attacked, plasticity is strongly developed. For example, the half-tension time of fibres at 40% extension is 11·7 minutes in *N*/100 sodium carbonate solution, compared with 114 minutes in water and over 1,000 minutes in *N*/10 hydrochloric acid.

As has already been mentioned, animal fibres possess perfect elasticity of form in water at ordinary temperatures, despite their plasticity. Even after being stretched 70% by slow loading in water (Table XIV), they return to their original length on being released in water. At humidities below saturation, however, extended fibres fail to return to their original length when released, as shown in Fig. 12 (Astbury and Woods, *l.c.*). The rate and extent of recovery increase with increasing relative humidity of the atmosphere and a fibre which fails to return to its original length at any (low) humidity, gives perfect recovery in water.

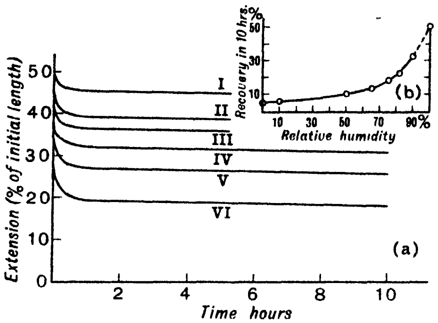


FIG. 12.

(*a*) Time/contraction curves of Cotswold wool fibres stretched to 50% extension and allowed to contract freely at constant humidity. I—10% R.H., II—50% R.H., III—65% R.H., IV—75% R.H., V—82·5% R.H., VI—90% R.H.

(*b*) The recovery after 10 hours of the fibres of Fig. 12 (*a*).

At raised temperatures, however, the elastic properties of animal fibres are peculiar. For example, when a wool fibre is kept at 41·3% extension in water at 86°C. for 30 minutes, and then released in water at 18°C., it fails to return to its original length: the extension after 75 minutes' release is 31·8% (Speakman, Trans. Faraday Soc. 1929, **25**, 169). This set is, however, eliminated when the fibre is immersed in water at 86°C.: after 151 minutes' immersion, the extension of the fibre is only 1·4%. The setting effect increases with rise of temperature, and a fibre which has been steamed or immersed in boiling water at any extension, shows little or no tendency to contract when released in *cold* water. Nevertheless, contraction does occur in steam (Speakman, *l.c.*). An exhaustive study of the phenomenon has been made by Astbury and Woods (*l.c.*). Wool fibres were steamed at 50% extension for various times and then released in steam until no further contraction took place. Their lengths were then measured, and the percentage extension or contraction of the various fibres is plotted against the time of steaming at 50% extension in Fig. 13. The curve shows that a fibre steamed for 2 minutes at 50% extension, although possessing a set permanent to *cold* water, can contract in steam to a length 30% ***less than the original length.*** X-ray photographs of the steamed, stretched fibres revealed attack on the side linkages between the peptide chains. Since Speakman (J. Soc. Dyers and Col. 1936, **52**, 335) has shown that various reagents, *e.g.* sodium bisulphite, silver sulphate and potassium cyanide, which are known to cause disulphide-bond breakdown, are capable of causing unstretched wool fibres to contract to a length less than the original length in aqueous solution at the boil, it seems clear that such contraction of stretched fibres in steam is associated with disulphide-bond breakdown. That system of main chain folding which is characteristic of α-keratin is clearly stabilised by the cystine and salt linkages: when the former linkages are broken down by steam or chemical reagents, further folding can occur, and the fibre contracts to a length less than the original length (super-contraction). When fibres are steamed at 50% extension for 15 minutes or longer, however, they fail to return to their original length when released in steam. It is apparent, therefore, that the primary process of disulphide-bond breakdown is followed by one of linkage rebuilding. The nature of this rebuilding process has been established by showing that fibres from which the amino groups have been removed by means of nitrous acid (deamination) are incapable of taking a permanent set even after steaming for 6 hours in the stretched state (Speakman, *l.c.*); and that the setting power of animal fibres (human hair) decreases in strict proportion to the amount of sulphur removed in the case of baryta-treated fibres (Speakman and Whewell, *ibid.* 1936, **52**, 380). Thus the new linkages which are responsible for true permanent set, *i.e.* set permanent to steam, are formed by interaction of the basic side-chains of animal fibres and the breakdown products of the cystine linkage. Since the first action of steam on the latter is to form a sulphinic acid:

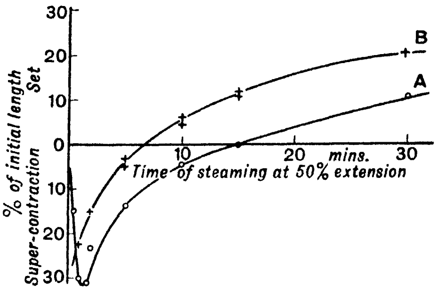


FIG. 13.

A. Normal fibres.
B. Irradiated fibres.

$$\mathrm{RCH_2{\cdot}S{\cdot}S{\cdot}CH_2R + H_2O} \\ \mathrm{= RCH_2{\cdot}S{\cdot}OH + RCH_2{\cdot}SH,}$$

one possible reaction scheme for linkage rebuilding is as follows:

$$\mathrm{RCH_2{\cdot}S{\cdot}OH + H_2NR_1} \\ \mathrm{= RCH_2{\cdot}S{\cdot}NHR_1 + H_2O.}$$

In keeping with this view, the linkages characteristic of permanent set were found to be stable in boiling sodium bisulphite solution, and set fibres were shown to contain free sulphydryl groups. Further, the facility with which stretched fibres assume a permanent set increases with rise of p_H up to 9·2, in the case of simple alkalis, as would be expected in view of the fact that disulphide-bond breakdown is an essential preliminary to the acquisition of set. Above p_H 9·2, there is a rapid decrease in the setting power of the fibres, due no doubt in part to decomposition of the sulphinic acid, which is known to be unstable in alkaline solutions: $RCH_2{\cdot}S{\cdot}OH = RCHO + H_2S$ (Schöberl, Annalen, 1933, **507**, 111; Collegium, 1936, 412). The aldehyde liberated in this way can, of course, react with the basic side-chains of animal fibres to form a second type of cross-linkage between the peptide chains:

$$RCHO + H_2NR_1 = RCH : NR_1 + H_2O.$$

Some such linkages have, in fact, been detected in fibres set at p_H 9·2 (Speakman and Stoves, J. Soc. Dyers and Col. 1937, **53**, 236), but the reaction can hardly be a primary one in setting processes, because so few $—CH : N—$ linkages are to be found in fibres set by means of sodium sulphite and sodium bisulphite, instead of simple alkalis. If $—S{\cdot}NH—$ bond formation is the primary reaction, the action of sulphites and bisulphites as setting agents is readily explained in terms of the following equations:

$$(1)\ RCH_2{\cdot}S{\cdot}S{\cdot}CH_2R + Na_2SO_3 = RCH_2{\cdot}SNa + RCH_2{\cdot}S{\cdot}SO_3Na$$

$$RCH_2{\cdot}S{\cdot}SO_3Na + H_2NR_1 = RCH_2{\cdot}S{\cdot}NHR_1 + NaHSO_3.$$

$$(2)\ RCH_2{\cdot}S{\cdot}S{\cdot}CH_2R + NaHSO_3 = RCH_2{\cdot}SNa + RCH_2{\cdot}S{\cdot}SO_3H$$

$$RCH_2{\cdot}S{\cdot}SO_3H + H_2NR_1 = RCH_2{\cdot}S{\cdot}NHR_1 + H_2SO_3.$$

In effect, therefore, a single reaction-mechanism serves to explain the action of alkalis, sodium sulphite and sodium bisulphite as setting agents, but side reactions leading to $—CH : N—$ bond formation are not to be excluded, particularly where the setting medium is alkaline.

(*c*) *Electrical Conductivity.*—As would be expected, the electrical conductivity of textile fibres increases with increasing relative humidity of the atmosphere, *i.e.* with increasing amount of adsorbed water (Murphy, J. Physical Chem. 1929, **33**, 200, 509; Murphy and Walker, *ibid.* 1928, **32**, 1761). The specific resistance of wool fibres is shown as a function of their water content in Table XVI (Marsh and Earp, Trans. Faraday Soc. 1933, **29**, 173).

TABLE XVI.

Relative humidity (%).	Water content (% on dry weight).	Specific resistance (ohms/cm.).
53	12	$1{\cdot}6 \times 10^9$
63	14	$1{\cdot}5 \times 10^8$
71	16	$2{\cdot}3 \times 10^7$
79	18	$6{\cdot}0 \times 10^6$
83	20	$2{\cdot}5 \times 10$
86	22	$1{\cdot}3 \times 10$

(*d*) *Thermal Conductivity.*—The thermal conductivity of textile materials and fabrics has been studied by many observers, but the results serve to show that the warmth properties of fabrics are due primarily to the low thermal conductivity of the air trapped in the fine capillary spaces between the fibres and threads. Both Sale and Hedrick (Technologic Papers of the U.S. Bureau of Standards, No. 266) and Speakman and Chamberlain (J. Text. Inst. 1930, **21**, T29) have derived expressions for the thermal resistance of wool fabrics in terms of their thickness and density. More recently, it has been argued (Cassie, King and Atkins, Nature, 1939, **143**, 163) that the warmth properties of textile materials in service on the human body may be accentuated by the fact that they adsorb water with evolution of heat. Thus, on passing from a warm, indoor atmosphere of low relative humidity to a cold, outside atmosphere of high relative humidity, the body does not experience a sharp change of temperature on account of the heat evolved by the textile fabric as it adsorbs water.

CHEMICAL PROPERTIES.

Water.—Besides being capable of severe attack on the strained disulphide bonds of animal fibres at 100°C., water causes disulphide-bond breakdown to a limited extent at 55°C. (Speakman, *ibid.* 1933, **132**, 930). In presence of light, however, the reaction between water and cystine linkages takes place rapidly at ordinary temperatures, sulphur being lost as hydrogen sulphide: $RCH_2{\cdot}S{\cdot}S{\cdot}CH_2R + H_2O = RCH_2SH + RCHO + H_2S$. The validity of this reaction scheme has been established by Speakman and McMahon (Trans. Faraday Soc. 1937, **33**, 844), who determined the acid and alkali titration curves of intact and exposed wools. On account of the presence of excess sulphydryl groups in the exposed wool, it possessed an increased affinity for alkali. The presence of aldehyde groups in exposed wool was established by qualitative tests, but quantitative determinations of aldehyde content were later carried out by condensing the wool with semicarbazide and *p*-bromophenylhydrazine (Race, Rowe, Speakman and Vickerstaff, J. Soc. Dyers and Col. 1938, **54**, 141). That the sulphur lost by wool during exposure to light and air is first liberated as hydrogen sulphide, has been established by Harris (J. Res. Nat. Bur. Stand. 1938, **20**, 563), who irradiated wool in an atmosphere of nitrogen. In air, however, the hydrogen sulphide undergoes rapid oxidation to sulphur dioxide and sulphuric acid (Meunier and Rey, Compt. rend. 1926, **183**, 596).

On account of such disulphide-bond breakdown in exposed wool, the latter swells to a greater extent than untreated wool in aqueous solutions (von Bergen, Textilber. 1923, **4**, 23; 1925, **6**, 745; 1926, **7**, 451) with the result that exposed wool is dyed more deeply than intact wool with colloidal dyes, and lighter than intact wool with crystalloidal dyes. Even if the primary acid dyeing is made level by using dispersing agents with colloidal dyes and excess acid with crystalloidal dyes, the dyeing becomes unlevel as regards hue on after-chroming. This further defect was found to be due (Race, Rowe and Speakman, J. Soc. Dyers and Col. 1938, **54**, 159) to the presence of excess reducing groups—aldehyde and sulphydryl groups—in exposed wool. The chromium deposited in exposed wool during after-chroming is more fully reduced than that deposited in intact wool, and a difference in hue results. A remedy for the defect was found (Race, Rowe and Speakman, *l.c.*) by pretreating the wool with a solution of basic chromium acetate in dilute acetic acid for 30 minutes at 40°C. before dyeing. The best chromium acetate for the purpose is the one which is one-third basic (*idem, ibid.* 1939, **55**, 69). When the inorganic polymer enters the fibre, it combines with the sulphydryl and other side chains, thus minimising the reducing properties of exposed wool. In addition, cross-linkages are formed between the peptide chains, and level acid dyeings can be obtained on wool containing exposed and unexposed fibres without resorting to modified dyeing conditions.

Disulphide-bond breakdown not merely causes increased swelling of wool fibres, but also promotes their solution. It is not surprising, therefore, that peptides pass into solution when wool is boiled in water (Gardner and Carter, *ibid.* 1898, **14**, 167), especially as peptide bonds may undergo hydrolysis under these conditions.

Acids and Alkalis.—Since the main peptide chains of wool are bridged by salt linkages (Fig. 5), the fibre is amphoteric. Speakman (*ibid.* 1925, **41**, 172) showed that combination with acid commences at p_H 4·8, and it was assumed that the isoelectric point of wool is at this p_H value. In the same year, Elöd (Z. angew. Chem. 1925, **38**, 837, 1112), using a different procedure, obtained an almost identical value, p_H 4·9, for the isoelectric point. Some disagreement was introduced by Meunier and Rey (Compt. rend. 1927, **184**, 285) when they found the swelling of wool to be a minimum at p_H 3·6–3·8, but the method of experiment was faulty. A revised procedure (J. Soc. Leather Trades' Chem. 1927, **11**, 285) showed minimum swelling at p_H 4·0–4·5, in closer agreement with Speakman and Elöd's values. Even the improved method of experiment did not give a precise measure of swelling, and there seemed to be no reason to doubt that the isoelectric point of wool is at p_H 4·8–4·9 until Harris (J. Res. Nat. Bur. Stand. 1932, **8**, 779) obtained a value of p_H 3·4 for the isoelectric point of wool by measuring the migration in an electric field of wool particles suspended in buffer solutions of various p_H values. Later, however, Harris accepted the value p_H 4·2 for the isoelectric point of wool particles, and p_H 4·5 for cortical cells and scales (*cf* Sookne and Harris, Text. Res., 1939, **9**, 437). He attributes the error of his first determination to the specific effect on wool of the phthalate buffers used, but Speakman and Stott (Trans. Faraday Soc. 1934, **30**, 539) failed to detect any difference between a phthalate buffer and a hydrochloric acid-sodium chloride solution, both at p_H 3·4, as regards their effect on the resistance of wool fibres to extension. In the light of this and other evidence (to be given later), there appears to be no reason to doubt that the point at which wool begins to combine with acid is at p_H 4·8–4·9. Whether this p_H value is to be regarded as an isoelectric point or not is discussed below.

In view of its importance in connection with dyeing processes, the combination of wool with acids has been studied by many observers, but the early data relate to wool which was not brought to p_H 4·8–4·9 before use, and combination was studied as a function of the concentration of the solution (Georgievics and Pollak, Sitzungsber. Kaiserl. Akad. Wiss. 1911, **120**, (2b), 465; Dietl, Kolloid-Z. 1914, **14**, 319; Fort and Lloyd, J. Soc. Dyers and Col. 1914, **30**, 5; Meyer, Textilber. 1926, **7**, 605). Using different wools adjusted to p_H 4·8, however, Speakman and Hirst (Trans. Faraday Soc. 1933, **29**, 148) and Speakman and Stott (*ibid.* 1934, **30**, 539) have determined the titration curves with hydrochloric acid. The results revealed no significant differences between wools, indicating that the fibre is constant in composition in at least one important respect, viz. its content of basic amino-acids. Maximum acid-combining capacity was observed at p_H 1, and, in agreement with Meyer's conclusion, the amount of acid combined was found to be 80 c.c. $N/1$ acid per 100 g. dry wool. This value is what would be expected in terms of Marston's data (Table X) for the content of arginine and lysine, and Harris' determinations of the amino-nitrogen content of wool (J. Res. Nat. Bur. Stand. 1935, **14**, 563). The behaviour of wool with other acids is, however, peculiar, as shown in Fig. 14 (Speakman and Stott, Trans. Faraday Soc. 1935, **31**, 1425). In keeping with Loeb's results for

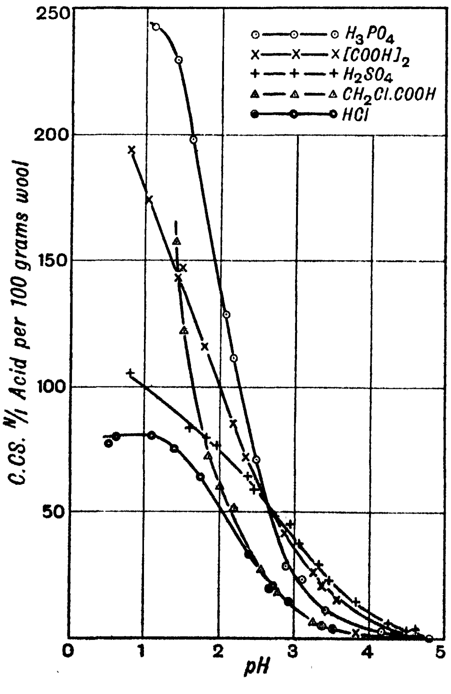


FIG. 14.—ACID-TITRATION CURVES OF WOOL.

proteins in general ("Proteins and the Theory of Colloidal Behaviour," McGraw-Hill Book Company, 1922, p. 40), oxalic and phosphoric acids tend to behave as monobasic acids, but the case of monochloroacetic acid is peculiar. Like other weak acids, it causes intense swelling of wool fibres when the solution is concentrated (Speakman and Stott, Trans. Faraday Soc. 1934, **30**, 539). Since this exceptional type of swelling is associated with a large amount of combined acid and a high heat of reaction (*idem, ibid.* 1938, **34**, 1203), it has been argued that all three phenomena are due to the separation of the superimposed sheets of covalently-linked peptide chains which form the micelles. The separation, which is due to the high swelling pressure developed in accordance with the Procter-Wilson theory (J.C.S. 1916, **109**, 307, results in the liberation of those —NH— groups for combination with acid which were at first associated with the —CO— groups of neighbouring peptide chains.

On account of their intense swelling in concentrated solutions of weak acids, wool fibres offer less resistance to extension in such solutions than in solutions of strong acids at the same p_H value (Speakman, Proc. Roy. Soc. 1931, A, **132**, 167; J. Soc. Leather Trades' Chem. 1933, 229; Speakman and Hirst, *l.c.*). Nevertheless, the reduction in the resistance of wool fibres to extension in solutions of hydrochloric acid is a linear function of the amount of combined acid, and is the direct effect of salt-linkage breakdown, which facilitates unfolding of the peptide chains during fibre extension. The small contribution made by swelling is evident from the fact that the maximum reduction in the resistance of fibres to extension in solutions of hydrochloric acid, containing salt in $N/5$ concentration as a swelling depressor, is no less than in solutions of hydrochloric acid in water. Support for this conclusion is to be found in the properties of de-aminated wool (Speakman and Stott, Nature, 1938, **141**, 414). Sookne and Harris' attempt (J. Res. Nat. Bur. Stand. 1937, **19**, 535) to refer the whole effect of acid to the induced swelling, rather than to the direct effect of salt-linkage breakdown, has been shown (Speakman, Amer. Dyestuff Rep. 1938, **27**, P168) to be erroneous.

In addition to simple combination with the basic side-chains of salt linkages, more complicated reactions may occur, especially at high temperatures, with certain acids. According to Harris, Mease and Rutherford (J. Res. Nat. Bur. Stand. 1937, **18**, 343), for example, a sulphamic acid is formed when wool is treated with a concentrated solution of sulphuric acid:

$$R{\cdot}NH_2 + H_2SO_4 \rightarrow R{\cdot}NH_3{\cdot}HSO_4 \rightarrow R{\cdot}NH{\cdot}SO_3H + H_2O.$$

The same reaction is presumed to occur when wool soaked in dilute sulphuric acid is dried at a high temperature, and the loss of basicity in the wool is assumed to be responsible for the resist effects against acid dyes, which are sometimes produced in the carbonising process. In offering this explanation, Harris and his collaborators overlooked the fact that tyrosine may be sulphonated in the cold by concentrated sulphuric acid, and most of the effects they observed can be explained equally well on this hypothesis. The case of nitric acid is even more complicated than that of sulphuric acid, and has not yet been examined in any detail. Finally, it should not be overlooked that boiling dilute acids are capable of hydrolysing the peptide bonds in the main peptide chains of wool, as would be expected from the fact that boiling 20% hydrochloric acid is used to dissolve wool for the purpose of amino-acid analysis.

The alkali-titration curve of wool was first determined by Speakman and Stott (Trans. Faraday Soc. 1934, **30**, 539) and it was found that little or no combination with alkali takes place below p_H 7. This result is in strict conformity with the observation of Speakman and Hirst (*l.c.*) that the resistance of wool fibres to extension in $N/5$ salt solutions containing various amounts of hydrochloric acid or caustic soda is independent of p_H between p_H 5 and 7. It was on the basis of this observation that Speakman and Hirst suggested that p_H 4·8 must not be regarded as an isoelectric point, but rather as one end of a p_H-stability region extending from about p_H 5 to 7. The titration curve of wool supports this view, and Elöd's failure to agree may be due to the fact that he has not taken account of the effects of disulphide-bond breakdown on the alkali-titration curve of wool. It has already been mentioned that when wool fibres are exposed to light and air, the disulphide bonds undergo hydrolysis and sulphydryl groups (cysteine side chains) are liberated. The titration curves of intact (root) and exposed (tip) sections of New Zealand Romney wool staples are shown in Fig. 15 (McMahon and Speakman, Trans. Faraday Soc. 1937, **33**, 846). On account of the presence of excess sulphydryl groups in the exposed wool, it possesses a greater affinity for alkali than intact wool at the same p_H value. In the light of these results, it seems probable that if Elöd were to apply his procedure to intact wool, it would be found to show an isoelectric region from about p_H 5 to p_H 7.

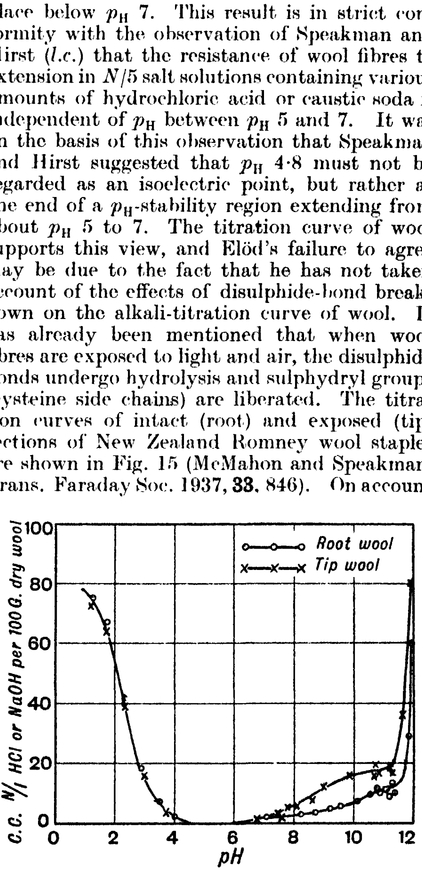


FIG. 15.—TITRATION CURVES OF INTACT AND EXPOSED WOOLS.

The affinity of intact wool for alkali is not due solely to the acid side-chains of salt linkages, because the disulphide bonds are attacked at high p_H values. For this reason, the titration curve at p_H values above 10 is valid only for the particular time of experiment employed. Harris (J. Res. Nat. Bur. Stand. 1939, **22**, 535) has made an attempt to determine the true limiting base-combining capacity of wool by working at 0°C. and correcting for the effects of disulphide-bond attack. He finds a value of 70 c.c. $N/1$ $NaOH$ per 100 g. dry wool, in fair agreement with the requirements of the salt-linkage hypothesis.

The nature of the decomposition undergone by cystine linkages in alkali appears to be similar to that caused by exposure to light and air (*see* p. 99*c*):

$$RCH_2{\cdot}S{\cdot}S{\cdot}CH_2R + H_2O = RCH_2SH + RCH_2S{\cdot}OH.$$

$$RCH_2S{\cdot}OH + NaOH = RCHO + NaSH + H_2O.$$

This view is in agreement with the work of Schöberl and Wierner (Annalen, 1933, **507**, 111) and is supported by Crowder and Harris' observation (J. Res. Nat. Bur. Stand. 1936, **16**, 475) that half the sulphur may be removed from wool by treatment with caustic soda solution in absence of oxygen.

Although the nature of the decomposition of disulphide bonds by alkalis such as barium and calcium hydroxides may differ from that caused by sodium hydroxide, sulphur is removed and aldehyde groups are formed in all cases. The fate of the aldehyde appears to be to combine with the basic side-chains of wool to form —$CH:N$— linkages between the peptide chains. This suggestion was made by Phillips (Nature, 1936, **138**, 121) to explain the action of amines in assisting the unhairing of skins by fresh lime liquors, and the effect of alkali treatment in opposing unhairing. Speakman (*ibid.* 1936, **138**, 327) has obtained evidence of the existence of —$CH:N$— linkages in fibres treated with caustic soda, and the function of the amines as unhairing assistants is obviously to prevent cross-linkage formation in the fibres by taking the place of the basic side-chains in condensation with the aldehyde. Besides the —$CH:N$— type of cross-linkage, some evidence has been obtained (Speakman, *l.c.*; Speakman and Whewell, J. Soc. Dyers and Col. 1936, **52**, 380) that —$C{\cdot}S{\cdot}C$— linkages are also formed when wool is treated with alkalis.

The peculiarities of the action of concentrated caustic soda solutions on wool at low temperatures were first revealed by Buntrock (Farben-Ztg. 1898, **9**, 69), who studied the effect of treating wool yarn with solutions of various concentrations. Each sample was immersed in caustic soda solution for 10 minutes at room temperature, and then freed from alkali by neutralisation with acid and washing in water. The strength of the dried yarn decreased continuously with increasing concentration of alkali up to 15% (g./100 g. solution) and then increased until a strength 30% greater than the original was attained with 38% caustic soda solution. Treatment of wool yarn with 38% caustic soda solution was therefore recommended as a "mercerising" process for increasing the strength and lustre of wool. It has since been shown by Speakman (J.S.C.I. 1929, **48**, 321T) that 38% caustic soda solution has itself no action on wool fibres, because it has the composition of the hydrate, $2NaOH,7H_2O$, and is used at a temperature near its freezing-point (15·5°C.). The increased strength and lustre realised by the "mercerising" process are due simply to surface attack on the fibres by the dilute alkali formed during neutralisation and washing-off.

Reducing Agents.—Alkaline reducing agents have a powerful destructive action on wool owing to disulphide-bond attack. To be effective, the p_H value of the solution should be at p_H 11 or above (Marriott, J. Soc. Leather Trades' Chem. 1925, **9**, 618), presumably because disulphide-bond hydrolysis precedes reduction. In the case of sodium sulphide, for example, the course of the reaction seems to be as follows:

$$RS{\cdot}SR + H_2O = RSH + RS{\cdot}OH.$$

$$RS{\cdot}OH + 2NaSH = RSH + Na_2S_2 + H_2O.$$

The liberated sulphydryl groups combine with alkali, a powerful swelling pressure is developed, and the fibre is gelatinised and dissolved. This is the basis of the unhairing process of the leather trade, where lime liquors are used as depilatories. Old lime liquors are superior to fresh liquors because they contain a reducing agent, calcium sulphide, derived from the action of lime on wool or hair in previous treatments. The calcium sulphide, by reducing the sulphinic acid as soon as it is formed, prevents its decomposition to give an aldehyde, and the —$CH:N$— cross-linkages which would oppose gelatinisation of the fibre are not formed.

Sulphur dioxide, sodium sulphite, sodium bisulphite and sodium hyposulphite also find industrial use as bleaching and stripping agents. King (J. Soc. Dyers and Col. 1930, **46**, 225; J.C.S. 1927, 2639; 1929, 601; B.P. 332389) found that sodium sulphite and sodium bisulphite are best used together in the proportions represented approximately by the formula $2NaHSO_3,Na_2SO_3$, and in such concentration that the SO_2 content of the solution is 2%. Since the p_H value of the solution is 6·8, the process has come to be known as the "neutral bleach." One of its merits is that it imparts a soft handle to the material, due no doubt in part to the action of the sulphites in causing partial breakdown of disulphide bonds:

$$RS{\cdot}SR + NaHSO_3 = RSNa + RS{\cdot}SO_3H.$$

A more common industrial bleach is that given by sulphur dioxide obtained by burning sulphur in a closed chamber containing the materials to be bleached. Having been soap scoured, the wool is originally alkaline, and exposure to sulphur dioxide causes the formation of sulphites in high concentration. A study of the process has been made by Phillips (J. Soc. Dyers and Col. 1938, **54**, 503), who has obtained conclusive proof of disulphide-bond breakdown with formation of S-cysteinesulphonate side-chains.

The damage caused by disulphide-bond breakdown with either acid or alkaline reducing agents may be repaired, to some extent at least, by after-treatment of the wool with either oxidising agents or salts of polyvalent metals (Speakman, *ibid.* 1936, **52**, 423). Treatment with reducing agents, followed by oxidising agents or metal salts, has also been made the basis of methods for imparting a permanent set to animal fibres at low temperatures (Speakman, B.P. 453700 and 453701).

Oxidising Agents.—Oxidising agents have a destructive action on animal fibres, such as wool and hair, owing to disulphide-bond attack. The action of hydrogen peroxide has been studied in some detail by Harris and his collaborators (J. Res. Nat. Bur. Stand. 1936, **16**, 301, 309; 1936, **17**, 577; 1937, **18**, 623; 1938, **20**, 555, 559) on account of its use in commercial bleaching processes. Under the correct conditions, the cystine content of the fibres decreases, even though the sulphur content remains unchanged. This is due to oxidation of the disulphide bond, presumably with formation of a disulphoxide. Since the latter is more readily hydrolysed than the disulphide, the alkali solubility of peroxide-treated fibres is greater than that of untreated fibres, and alkaline hydrogen peroxide is particularly destructive in its action on wool. In commercial practice, however, little control appears to be exercised over the p_H of peroxide-bleaching baths (Weber, J. Text. Inst. 1933, **24**, P178).

More powerful oxidising agents, *e.g.* chlorine peroxide, are capable of oxidising cystine to cysteic acid (Schmidt and Braunsdorf, Ber. 1922, **55**, [B], 1529; Schmidt, Haag and Sperling, *ibid.* 1925, **58**, [B], 1394), and wool treated with this reagent can be dissolved readily by such solvents as are normally used to dissolve silk.

Halogens.—Chlorine and bromine have a particularly destructive action on the disulphide bond in presence of water (Douglass and Johnson, J. Amer. Chem. Soc. 1938, **60**, 1486), and the use of chlorine water or hypochlorous acid to impart an unshrinkable finish to wool is based on this reaction. The process has been studied by numerous observers (Trotman, J.S.C.I. 1922, **41**, 219T; 1926, **45**, 20T, 111T; Speakman and Goodings, J. Text. Inst. 1926, **17**, T607; Edwards, J.S.C.I. 1932, **51**, 234T). According to Speakman and Goodings, the unshrinkable finish is due to the fact that the surface scale structure of the chlorinated fibres is rendered inoperative, as regards shrinkage, by a layer of jelly which is formed as soon as the attacked structure is treated with alkali (soap and soda). Such gelatinisation is due, of course, to the action of chlorine in causing disulphide-bond breakdown. Attack should be restricted to the surface of the fibre, since the surface scales are responsible for shrinkage (Speakman, Stott and Chang, J. Text. Inst. 1933, **24**, T273), but this is difficult of realisation when aqueous solutions of chlorine are used. The Wool Industries Research Association, King and Galley (B.P. 417719) have, however, taken advantage of the inaccessibility of dry fibres to reagents the molecules of which are larger than the *n*-propyl alcohol molecule (Speakman, Trans. Faraday Soc. 1930, **26**, 61) to ensure surface reaction: chlorine is applied as a gas to wool of low water content, with successful results. In a still more recent process (Hall, Hicking and Pentecost, B.P. 464503) surface reaction and an unshrinkable finish are realised by treating wool with a solution of sulphuryl chloride in white spirit. The disulphide bonds are attacked in much the same way as with chlorine, for it has been shown (Speakman, Nilssen and Elliott, Nature, 1938, **142**, 1035) that dibenzyl disulphide is converted into benzylsulphonyl chloride and benzyl chloride by treatment with a solution of sulphuryl chloride in ether at a low temperature.

Although the main point of attack by halogens is the cystine linkage, the reaction with animal fibres is complicated and the possibility of attack on peptide bonds and tyrosine side-chains should not be overlooked (Stirm and Collé, Textilber. 1935, **16**, 585, 667, 795; vom Hove, Angew. Chem. 1934, **47**, 756; Haller and Holl, Textilber. 1936, **17**, 493).

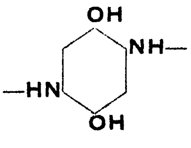
Inorganic Salts.—Chief among the inorganic salts used in commercial practice on wool must be ranked the chromates and dichromates. Applied to wool from neutral or acid solution, and in presence or absence of reducing agents, oxides of chromium are deposited in the fibres to serve as mordants in dyeing processes. The chromic acid at first combined with the basic side-chains of the fibre is reduced, either by disulphide-bond attack, or by the reducing agents present in the mordanting bath.

Disulphide-bond attack is also the basis of the use of mercuric nitrate and nitric acid in the carrotting process for increasing the felting power of rabbit and hare fibres. Mercuric chloride in acid solution likewise promotes disulphide-bond breakdown at temperatures above 40°C. (Speakman and Coke, Trans. Faraday Soc. 1939, **35**, 246) according to the equation:

$$\mathrm{RS{\cdot}SR + HgCl_2 \rightarrow RSCl + RS{\cdot}HgCl.}$$

Similarly, the use of thiocyanates for shrinking (crêping) wool textile materials, is due to the fact that under slightly alkaline conditions, the steaming process gives rise to hydrosulphides, which, as indicated above, cause disulphide-bond breakdown and super-contraction (Justin-Mueller, Rev. Gén. Mat. Col. 1937, **41**, 419).

Organic Compounds.—The reactivity of wool with organic compounds has been studied only to a very limited extent, owing mainly to the fact that the dry fibre is accessible only to compounds of low molecular weight. Such swelling agents as can be used to increase accessibility viz. water, methyl alcohol, ethylene glycol, formic acid and acetic acid, are themselves reactive with the compounds which might be expected to attack wool. Animal fibres can, of course, be acetylated, with reduction in their affinity for acid dyes, but details of the commercial process are not available. Phosgene combines with the basic side-chains of wool to give —N:CO side-chains, and formaldehyde and quinone condense with the amino groups of the same side-chains. In the last case, cross-linkages of the following type:



are formed between the peptide chains (Speakman and Coke, *l.c.*), but the reaction is complicated and all its features have not yet been elucidated.

J. B. S.

FIBRES, ARTIFICIAL, or RAYON.

The idea of imitating silk with artificially produced fibres is an old one, being mentioned in 1665 in Hooke's "Micrographia," p. 7, and again in 1734 in Réaumur's "Histoire des Insectes," I, 154. However, it was not until the nineteenth century that there was any record of the actual production of artificial fibres.

Contemporaneously with the starting of the first practical processes of manufacture, the term "artificial silk" was coined in 1885. About this time the high price of real silk, which was not less than 16*s.* per lb. from 1900 till 1930 (Flügge, "Rohseide," Bibliograph. Inst. A.G. Leipzig, 1936) was no doubt the inducement to attempt its imitation. But since then steadily falling costs of production and increasing technical skill have made it possible to imitate other fibres, so that the term "artificial silk" has gradually become more inapt. Besides this it was felt, even before the war (1914–18) that "artificial silk" was an unworthy name for a product which had a claim in its own right to a place among the textile fibres (Douglas, J. Soc. Dyers and Col. 1914, **30**, 178). The term "rayon" which was coined in America as the result of a competition in 1924, has been substituted as the generic name. It was stated recently that "rayon" properly describes all types of "synthetic" fibres whose basic raw material is cellulose (Rep. on Dev. and Use of Rayon and Other Syn. Fibres, Dept. of Agric. U.S.A. 1938), but the term is generally used to describe artificial and synthetic fibres whether made from cellulose or not, although it should be mentioned that the British Celanese Company has not accepted the term as applied to their product (Text. Manuf. Suppl. May, 1936, p. xxxv).

Recently new synthetic fibres have been produced by Du Pont de Nemours in the United States, which appear to be the first true artificial silk, since not only in appearance but also in physical and chemical properties they are similar to silk. It must be remembered that similar claims have been advanced in the past and have not been substantiated, but the claims of the new fibres ("*Nylon*") appear more securely grounded. If they prove as satisfactory as is claimed, there may be an important repercussion in the Japanese–United States trade in natural silk since Japan's silk exports are about 15% of her total exports and about 80% of her silk exports are taken by the United States.

Continuous Filament Rayon Yarns.—The production of continuous filaments by artificial means began in France in 1889, following quickly in Germany and England, but American production did not begin until 1911, Italian until 1913 and Japanese until 1922. However, in spite of their late starts the United States and Japan are now the leading producers, being responsible together for 47% of the total world production in 1938 ("Industrial Fibres," H.M.S.O. 1939).

World Production of Rayon and Other Fibres.

Year.	Continuous filament rayon.	Rayon staple fibre.	Silk.	Wool.[1]	Flax.	Cotton.
	Million pounds per annum.					
1900	2[2]	0	37[4]	.		...
1910	18[2]	0	50[4]	1,770[5]	–	10,500[6]
1920	55[2]	1[2]	43[4]	–	—	10,000[6]
1930	453[3]	6[3]	130[3]	2,200[3]	1,400[3]	12,400[3]
1938	991[3]	982[3]	110[3]	2,240[3]	1,760[3]	14,000[3]

[1] Values shown are 57% of the greasy wool clip.

[2] Flügge, "Kunstseide," Bilbiograph. Inst. A.-G. Leipzig, 1936.

[3] "Industrial Fibres," H.M.S.O. 1938 and 1939.

[4] Flügge, "Rohseide," Bibliograph. Inst. A.-G. Leipzig, 1936.

[5] "Survey of Textile Industries," H.M.S.O. 1928.

[6] Year Book, National Assoc. of Cotton Man., Boston, U.S.A. 1927, p. 261.

The rate of increase of world production of rayon has been 20% per annum, with slackenings corresponding to the war (1914–18), the economic crisis of 1929 and the over-production in 1937.

An important cause of the increased consumption which has absorbed the increased production has been the fall in yarn prices which has occurred since 1918. In England 150 denier[1] viscose rayon prices rose from 5*s.* 3*d.* per lb. in 1913 to a peak of 19*s.* 3*d.* per lb. in February, 1920, but have since fallen steadily having reached 6*s.* per lb. by 1927 ("Survey of Textile Industries," H.M.S.O. 1928, p. 304). Subsequently prices continued to fall until by 1933 they had reached 3*s.* 6*d.* per lb., at which time acetate rayon had fallen to about the same price as viscose, though previously it had been considerably dearer. In the winter of 1938 viscose yarn prices reached a minimum at 2*s.* 6*d.* per lb. for 150 denier 27 filament viscose yarn on pirn ("Industrial Fibres," H.M.S.O. 1939), but since then there has been a tendency for prices to rise again. The price was 2*s.* 10½*d.* per lb. in February, 1940, for normal viscose, but the prices of Courtaulds strong yarn, "*Tenasco*," and of Celanese strong yarns, M and MV, are higher. During the period under consideration there have been two price changes imposed on the industry; an excise duty of 1*s.* per lb. introduced in 1924, and its subsequent reduction to 6*d.* per lb. in July, 1934. Silk, wool and cotton prices at their different levels have shown similar trends to rayon prices in the period 1913–38. American rayon prices rose from 1·90 dollars per lb. in 1911 to a peak of 4·77 dollars per lb. in 1919, and since then have fallen, at first rapidly and afterwards more slowly (E. Flügge, "Kunstseide," Bibliograph. Inst. A.-G. Leipzig, 1936) to a minimum at 0·49 dollars per lb. in the summer of 1938 for first quality viscose yarn ("Industrial Fibres," H.M.S.O. 1939). The price of nylon in December, 1939, was 3·25–4·55 dollars per lb. for hosiery knitting yarns and was only very slightly less than the price of similar silk yarns (Textile World, 1940, **90**, No. 1, 52).

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[1] The denier count of artificial silk yarn is the weight in grams of 9000 metres.

Yarn prices, which in turn have been controlled to a large extent by production costs, have been one of the main factors which have affected the fortunes of the different rayon processes. The other factors have been general wearing qualities and the ability to produce novelty effects.

At the end of the nineteenth century the Chardonnet nitrate process accounted for more than 80% of the world's production, but even then it was beginning to lose its pre-eminence, the decline proceeding steadily until production appears to have ceased altogether in the middle of the nineteen-thirties. This was brought about in the first instance by the superior product and cheaper costs of the cuprammonium process, for it was not until as late as 1909 that there was recovery of the costly solvents used in the nitrate process (J. Soc. Dyers and Col. 1909, **28**, 1303). During the first few years of this century the cuprammonium process was gaining ground at the expense of the Chardonnet process until in 1906 the former accounted for 40% of the total world production. Subsequently the cuprammonium process was subjected to the competition of the cheaper viscose process and by 1923 declined to a mere 2% of the total output, though this proved to be its nadir, for subsequently production rose again and has maintained a fairly steady position at 3–4% of the total production by all processes. The reason for the maintenance of its relative position is to be explained by the high quality of cuprammonium yarns.

After 1906, production by the viscose process started to rise rapidly, reaching a peak of 87–88% of the production by all processes in the period 1932–34, though subsequently there has been a slight decline to 83% in 1938. This decline has been caused by the rise of the acetate process and can be accounted for by the special properties of acetate yarns, which enable special textile effects to be produced which can be obtained in no other way. Large scale production of acetate yarns began as a result of the requirements during the war (1914–18) of acetate dope for aeroplanes. The producers found themselves faced after the war with the problem of disposing of their dope production. In 1920 the manufacture of yarns from this dope began and has since risen steadily to 13% of the world production by all processes in 1938, although probably in England and certainly in North America the production by this process is a much higher proportion of the whole. In 1939 small samples of yarns made from polyvinyl chloride and of nylon became available and Du Pont de Nemours & Co.'s large scale plant for the manufacture of the latter began operation in the United States on December 15, 1939 (Textile World, 1940, **90**, No. 1, 52). The English plants are to be operated jointly by Courtaulds and I.C.I. through a subsidiary company, British Nylon Spinners, Ltd., and are expected to start producing in the autumn of 1940 (*Times*, March 15, 1940, p. 3). I.C.I. are to produce the polymer at their Huddersfield works and this is to be spun into monofil at Welwyn Garden City and into yarn at Coventry (*Times*, March 21, 1940, p. 5).

Rayon Staple Fibres.—Initial interest in the manufacture of staple fibres arose in Germany during the war (1914–18) when it became necessary to eke out slender supplies of natural staple fibres. Demand and production languished when normal supplies were restored after the war was over. German production of 4·2 million lb. in 1919 fell to 1·3 million lb. in 1920 (Königsberger, "Die deutsche Kunstseiden-und Kunstseidenfaserindustrie in den Krieg-und Nachkriegsjahren," Berlin, 1925). About 1930 interest in artificial staple-fibres revived, partly because of improvements in manufacture which resulted in increased strength, and since then there has been a more than hundred-fold increase in production. The principle producers are Germany, Italy and Japan, who as part of their national policies of self-sufficiency have encouraged the production of these fibres and recently have even passed regulations to enforce their use: a German decree in 1935 enforced the admixture of at least 8% rayon staple-fibre in all coarse cotton yarns; this proportion being raised in 1937 first to 16% and then to 20%. Similarly Japanese decrees in 1938 required first a minimum admixture of 30% rayon staple-fibre with all cotton for domestic use (with certain exceptions) and then prohibited the use of cotton altogether, whilst decreeing that 50% of rayon staple-fibre must be mixed with all wool used ("Rep. on Dev. and Use of Rayon and Other Syn. Fibres," U.S.A. 1938). Recently Italy has decided that all textiles for her home markets must contain at least 20% of home-produced artificial fibres, the woollen industry being expected to use them in the form of "*Lanital*" and "*Cisalfa*" fibres (*Times*, March 21, 1939). Probably because of the influence of these decrees, Japanese, German and Italian production together accounted for about 90% of the total world production in 1938 ("Industrial Fibres," H.M.S.O. 1939). A still greater increase in German production is envisaged by Schieber (*Times*, February 14, 1940).

Unlike continuous filament rayon, which in the first instance can be considered a cheap substitute for expensive natural silk, rayon staple-fibre is, again in the first instance, a substitute for the comparatively cheaper cotton and wool fibres. Consequently in order to popularise its use in those countries where its use has not been compelled by law, the manufacturers have progressively reduced its price. This trend was accelerated in England by the reduction of the 6*d*. a lb. excise duty imposed in 1924 to 3*d*. a lb. in June, 1934, and then by its complete abolition in September, 1935. In 1936 the price of viscose staple-fibre was 11*d*. per lb., but this was reduced to 10*d*. per lb. at the end of 1937 and there was no further change until the end of 1939 when there was a slight tendency for the price to rise. In February, 1940, it was 12½*d*. per lb. Acetate staple-fibre has generally been about 50% dearer than viscose.

In the United States viscose staple-fibre prices fell steadily from 1928 when the price was 0·60 dollars per lb. to 1937 when the price was 0·25 dollars per lb. Here again acetate prices have been higher than viscose prices, though they fell from 0·80 dollars per lb. in 1936 to 0·46 dollars per lb. in 1938 (" Rep. on Dev. and Use of Rayon and Other Syn. Fibres," U.S.A. 1938).

No reliable statistics are available for the proportions of rayon staple-fibres made by the different processes, though it is probable that the viscose process, including such modifications as the processes for producing basified viscose fibres, is responsible for 90–95% of the total production. Fibres made from casein probably amount to no more than 1–2% of the whole, whilst a not inconsiderable though relatively small amount of acetate staple-fibre is produced.

MANUFACTURE OF RAYONS.

Substances that can be formed into filaments must have linear molecules and high molecular weights and, up to now, all fibre-forming molecules have been of the superpolymer type in which there are many hundreds of repetitions of a comparatively simple chain unit. A number of natural substances have suitable molecular structures but the processes used to form these into fibres invariably cause some measure of depolymerisation. However, there have been several successful attempts recently to synthesise substances capable of forming fibres by the polymerisation or condensation of small molecules into long chains. For rayon manufacture fibre formation is not sufficient. Only those substances are suitable for rayons that will form fibres with desirable textile properties. The most important of these properties are: strength, extensibility, flexibility and insolubility in water and dilute alkalies. The fibres must also be non-inflammable, have a high softening point and be capable of being dyed. In addition it is preferable, though not essential, that the fibres be truly elastic. Finally there is the over-riding economic consideration that new artificial fibres must be produced more cheaply than the natural fibres or older artificial fibres with which they have to compete. Only a few natural and synthetic substances give fibres which satisfy all these requirements.

In the broadest possible terms the processes of rayon manufacture consist of liquefaction of the fibre-forming substance and extrusion of this as filaments which are subsequently solidified. Generalising again, the capital difficulty of rayon manufacture is the attainment of uniformity. This statement should perhaps be qualified in the case of rayon staple-fibres, since these can be blended like cotton or wool, but no such levelling of inequalities can be applied to continuous filaments. Continuous-filament rayon from its nature has a comparatively uniform and regular form, so that any irregularity, in particular any periodic irregularity, is strikingly obvious. A similar irregularity would probably pass unnoticed among the sporadic irregularities inherent in staple-fibre yarns. For this reason a perfectly uniform rayon yarn which is slightly defective in other ways is preferable to a rayon yarn which is irregular though free from other defects. A perfectly uniform rayon yarn can be obtained only by perfectly uniform chemical and mechanical processes.

With rayon staple-fibres, strength, elasticity and special dyeing properties have a greater importance than with continuous-filament rayons, since rayon staple is intended to blend with or even substitute strong fibres like cotton and flax and elastic fibres like wool and schappe silk. For similar reasons the staple length and denier of cut rayon fibres must be suitable for the spinning machinery in the cotton and wool industries.

Many processes have been proposed for improvements in the manufacture of rayons, but in the space available it is only possible to consider the more important processes. These are described as far as is practicable in the order of historical development since in the writer's view, this brings out most clearly the sequence of the ideas and the growth of the refinements which have brought the industry to its present great position.

MANUFACTURING PROCESSES.

Glass Fibres.—The earliest artificial fibres to be produced were made from glass and it is recorded that these were exhibited at the British Association meeting held in 1842 (Hard, " The Romance of Rayon," Manchester, 1933). Yarns made from glass fibres have been woven into textile fabrics, but these do not appear to have passed the stage of technical curiosities. Modern glass fibres are very fine and yarns made from them are extremely strong and quite flexible (Lindsay Forster, J. Text. Inst. 1939, **30**, P162), however their comparative hardness would be a serious disadvantage if glass yarns were to be used in combination with other textile fibres. They are at present used only in filter cloths and for electrical and thermal insulation. Modern glass fibre yarns have tensile strengths as high as 6·3 g./den., but have elongations of only 1–2% (Textile World, 1939, **89**, No. 10, 76).

Cellulose Nitrate Process.—Although (in 1838) Pelouze had noticed that concentrated nitric acid appeared to form a compound with cotton, it is probably to Schönbein's discovery of " guncotton " (Phil. Mag. 1847, **31**, 7) that the chief credit should be given for the discovery of cellulose nitrate. This was found by Ménard in 1846 and independently by Maynard in 1848 to be soluble in a mixture of ether and alcohol giving a solution known as " collodion," the transparent films from which were used in photography from 1850 onwards. The publicity that cellulose nitrate received from its many important applications, and the fact that it was the first substance suitable for forming fibres to become readily available, are doubtless the reasons why the first rayon process patented was the cellulose nitrate process of Audemars (B.P. 283, 1855). His process showed a curious connexion with sericulture in using mulberry bast fibres as the raw material. Filaments were formed by dipping steel spikes into the collodion and then withdrawing them upwards so that the fine streamers of solution formed filaments by evaporation of the solvent. This crude method was superseded through the introduction of single hole spinnerets suggested by Ozanam (Compt. rend. 1862, **55**, 833).

Audemars' patent marks the beginning of the experimental period which extended to 1889, in which year Count Chardonnet started the first rayon factory at Besançon (J. Soc. Dyers and Col. 1914, **30**, 199). Between 1884 and 1893 Chardonnet took out a large number of patents in France, England, Germany, America and Switzerland. From these patents it appears that the early spinning machines were arranged so that the collodion was extruded upwards through a row of single hole spinnerets, first into water and then into a chamber where the solvent was evaporated by means of a counter-current of hot air. The filaments were hardened in this chamber and groups of filaments were led upwards and collected on rotating spools.

In spite of the addition of various fireproofing substances (G.P. 38368 Cl. 29) this rayon was highly inflammable, and was called " mother-in-law silk " by the textile workers of Lyons who said a man could rid himself of his mother-in-law by presenting her with a dress made of this material (J. Soc. Dyers and Col. 1914, **30**, 199).

Sir Joseph W. Swan had also been working independently on the production of filaments from cellulose nitrate (J.S.C.I. 1885, **4**, 34), but for electric lamp filaments, and he had devised a process of denitration (with ammonium hydrosulphide) for the production of regenerated cellulose filaments (B.P. 5978, 1883). This process was subsequently adopted by Chardonnet and was the means of saving his yarns from proscription on the grounds of their inflammability (Hard, *op. cit.*), unfortunately whilst denitration reduces the fire hazard, it has the defect that it weakens the rayon since it produces serious degradation of the cellulose (Davidson, J. Text. Inst. 1938, **29**, T208).

In 1891 the production of the Besançon factory was only about 40,000 lb. per annum, but it showed a thirty-fold rise in the next thirteen years. After 1905, although production in France, Belgium and elsewhere continued to increase slowly for a time, the competition of first the cuprammonium process and then the viscose process was too great and production appears to have ceased altogether in the middle of the nineteen-thirties.

Protein Fibres.—The protein character of silk made it obvious that attempts would be made to produce fibres from other proteins. The earliest patent was that of Hughes (B.P. 67, 1857) which claimed that artificial fibres could be produced from a complicated mixture of which gelatine was one constituent. The next attempt was that of Ozanam (*l.c.*) who spun filaments from solutions of natural silk.

Much later Millar (B.P. 15522, 1894) described the production from gelatine solutions of silk-like filaments by evaporation of the solvent as they were carried on long travelling bands. Subsequently the filaments were insolubilised by treatment with formaldehyde, thus foreshadowing the present-day method of insolubilising protein fibres. Millar's " *Vanduara* " rayon was actually produced (*Glasgow Herald*, January 6, 1898) and from small samples still extant, it appears to have been an attractive product. Its strength was, however, very poor even compared to the low strengths customary for rayons at that period, also it had little extensibility. In 1903 Hassack, quoted by Dreaper (J.S.C.I. 1909, **28**, 1297), gave the strength as 0·63 g./den. and the extensibility as 3·5%. In a later patent (B.P. 6700, 1898) Millar proposes to use other proteins, including casein, for the production of artificial filaments, but his evaporative method of spinning was less suitable for the solutions he used than for the volatile solvent solutions employed by Chardonnet. Non-volatile solutions are better suited to wet spinning and Todtenhaupt (B.P. 25296, 1904, G.P. 170051) was the forerunner of the modern practice of spinning alkaline aqueous solutions of casein into an aqueous acid coagulating bath, which contained formaldehyde to harden and insolubilise the filaments.

Neither Todtenhaupt's process nor any of the numerous processes that were described in the patent literature during the next 30 years found large scale commercial utilisation until Ferretti's process (B.P. 483807; 483808; 483809; 483810; 510131; 511160) was adopted by the Snia Viscosa Company in Italy. This company began casein-fibre production in 1936.

According to Ferretti's specifications the casein is prepared from milk by coagulation with acid at p_H 4·5. (The isoelectric range of casein is p_H 3·5–6. Lloyd and Shore, " The Chemistry of the Proteins," London, 1938, p. 416.) A solution is then made by dissolving this casein with the aid of 23 litres 35° Bé caustic soda for every 100 kg. of casein, the solution afterwards being diluted until it contains 100 kg. of casein in 400 litres of solution. This solution is allowed to mature at 24°C. until the viscosity has fallen sufficiently, at which stage the maturation may be halted by cooling. The solution is spun by extrusion into a coagulating bath containing sulphuric acid, sodium sulphate and aluminium sulphate, the insolubilising action of the aluminium being assisted by a subsequent treatment in a bath containing formaldehyde, together with the addition of sodium chloride to diminish swelling in the bath. As with other rayons stretch-spinning is stated to improve the strength.

The aluminium and formaldehyde are each supposed to form cross-links binding the protein chains together (Diamond and Wormell, J. Text. Inst. 1939, **30** P224) and give the structure greater stability than it would have if this were to depend on the salt bridges formed by the lysine and glutamic acid side-chains alone. Additional ways have been proposed of improving the wet strength of the fibres, thus Courtaulds, Ltd. and Wormell (B.P. 495885) propose to acetylate the casein with one or other of a number of acetylating agents.

Fibres from soya-bean protein are being produced commercially on a small scale in Japan under the name of " *Silkool* " (B.P. 502047; 502048). Like casein fibres they have comparatively poor tensile properties, a breaking strength of 0·5 g./den. and an extensibility of 3–16% (Sakurada, J. Soc. Chem. Ind. Japan, 1939, **42**, 191B).

In spite of the many attempts to produce artificial protein fibres that should resemble silk, the inferior mechanical properties of these fibres have always prevented their use as substitutes. The fibres made by the Ferretti process, the only successful process to date, are no exceptions, since they cannot be used alone satisfactorily but must be used in admixture with other fibres, for example with wool. Had it not been for the effort to attain economic self-sufficiency in Italy, which imports considerable quantities of wool, it is doubtful if there would have been much progress in the manufacture of casein fibres. As it is there was a production of more than 3 million lb. in 1937, and more than 10 million lb. in 1938. They are also being made in small quantities in England by Courtaulds, Ltd., and in Holland by the A.K.U.

Although the actual amino-acid composition of casein is different from that of wool (Lloyd and Shore, "Chemistry of the Proteins," London, 1938, p. 136) both are proteins and possess similar dyeing properties, though generally casein fibres dye more rapidly than wool (Grundy, J. Soc. Dyers and Col. 1939, **55**, 345). However casein fibres are much more sensitive to hot aqueous treatments than are wool fibres, and particularly in the presence of dilute aqueous alkalis, casein fibres become plastic above 90°C.

Although, like wool, casein fibres have considerable extensibility, unlike wool they have inferior elasticity (Heim, J. Text. Inst. 1939, **30**, P213). In spite of this and in spite of the absence of scales from the surface of casein fibres, when mixed with wool they improve the felting properties of the latter, although alone they possess no felting properties (Diamond and Wormell, *l.c.*).

Cuprammonium Process.—The fact that cuprammonium hydroxide was a solvent for cellulose was discovered accidentally in the course of other work by Schweizer (J. pr. Chem. 1857, [i], **72**, 109). No application of this discovery was made until towards the close of the nineteenth century when a number of inventors, of whom Despaissis (F.P. 203741, 1890) was the first, devised processes to utilise Schweizer's discovery for the manufacture of rayons. In Despaissis's process the solution of cellulose in cuprammonium hydroxide was extruded through spinnerets and coagulated in a dilute acid bath. Unfortunately Despaissis did not live to develop his ideas and the cuprammonium process languished for a number of years until almost simultaneously Pauly (B.P. 28631, 1897), Fremery and Urban (B.P. 6557, 1899) and Bronnert (B.P. 13331, 1899) specified the conditions necessary for successful manufacture. These three patents describe the precautions to be adopted in preparing the cellulose solution. Both in Bronnert's and in Fremery and Urban's patents it is recommended that the cellulose be partially degraded to obtain solutions less viscous than those from undegraded native celluloses.

In 1898 the Glanzstoff Company began producing cuprammonium yarns in Germany according to the processes of these early workers. Later the same company operated a works in Wales which was taken over by Courtaulds, Ltd., during the war (1914–18) and converted to viscose production.

At the present time the cuprammonium process stands third in order of production. It is being worked in England, in America and on the Continent.

Cotton linters are used as the source of cellulose, these are kier-boiled and then bleached in large hollanders to remove impurities and to depolymerise the cellulose somewhat so as to obtain reasonably fluid solutions at useful concentrations. After bleaching, the linters are washed and hydroextracted preparatory to dissolving them in cuprammonium hydroxide solution. The cuprammonium solvent can be made in several ways and it is known that it has better solvent powers the higher the copper content and the lower the content of anions other than hydroxyl or carbonate. However, the solvent power of a cuprammonium solution containing acid ions can be improved by the addition of caustic soda.

The spinning solution may be prepared by mixing together the bleached cotton linters, ammonia, basic copper sulphate and caustic soda solution to obtain a 7% cellulose solution. In the absence of air and light this solution is perfectly stable and it can be spun immediately after it has been filtered. The filtration, however, need not be through such fine filters as with viscose or cellulose acetate solutions since the spinneret holes used are so much larger in this process. This is convenient since only inorganic filter materials such as fine nickel gauze can be used because of the solvent power of the solution on organic fibres.

Although Lehner (G.P. 58508 Cl. 29, 1890) had invented a process of stretch-spinning for cellulose nitrate filaments, it does not appear to have had the same success as Thiele's stretch-spinning process (B.P. 8083, 1902) in the cuprammonium method of making rayon. By means of Thiele's invention spinneret holes of 1 mm. diameter could be used and yet fine filaments could be produced. This was made possible because the setting of filaments was carried out very slowly in hot water, instead of rapidly in an acid, and during this slow setting the filaments could be stretched to many times their original lengths. By this device filaments finer than 0·12 denier could be produced and yarn with filaments finer than 1 denier was sold in England during the first decade of this century (Dreaper, J. Soc. Dyers and Col. 1937, **53**, 436). Not only did stretch-spinning permit finer filaments to be made than those that could be produced by any other process, but because of the better and more uniform orientation of the cellulose chains brought about during the stretching and the comparatively small degradation of the cellulose in the process as a whole, stronger yarns were produced than by other rayon processes. This unique position has changed, for viscose and acetate can now be stretch-spun, and highly stretched, and highly polymerised cellulose rayons produced from viscose and acetate are now made commercially.

Filtered cuprammonium-cellulose solution is forced along pipelines under pressure to the spinning room, where the pipes subdivide to feed the different spinning machines. Because of the large spinneret holes used, unlike those used in the viscose and acetate processes, individual spinning pumps are not necessary and one spinning pump can be used to a group of spinnerets. The spinnerets are made of stainless steel and have the holes arranged in a single circle. The holes are 0·8–1 mm. in diameter.

A modern version of Thiele's stretch-spinning arrangement is shown in G.P. 421339, Cl. 29a in which each of the spinnerets is immersed in the preliminary coagulating bath of water at 40–50°C. contained in a glass cylinder which has a coaxial glass funnel inside it. The hot water enters at the bottom of the cylinder and flows upwards in the annular space till it reaches the top of the funnel. The water then flows down the funnel with a velocity that increases as the diameter of the funnel decreases. The filaments extruded from the spinneret, which is mounted just above the mouth of the funnel, are carried down the funnel by the stream of water. As they travel down the funnel the filaments are gradually coagulated by the diffusion of the hydroxyl ions out of the filaments and at the same time the acceleration of the stream of water due to the narrowing of the funnel stretches the filaments. The coagulated filaments emerge from the bottom of the funnel together with the stream of water which is allowed to fall downwards whilst the filaments are carried to one side as in B.P. 284618. In the machine described in this patent the filaments next pass through a combined guide and acid bath, where they are treated with dilute sulphuric acid which neutralises the alkalinity and dissolves out the copper. After this the filaments are collected in an untwisted state on an acid-proof swift. Alternatively the filaments may be twisted and collected in a spinning pot (B.P. 299038).

It is interesting that Fremery and Urban (B.P. 6735, 1899) comment on the troubles attendant on bobbin spinning, which they say is owing to the contraction on drying of the jelly-like wet filaments. This difficulty has been the bugbear of all bobbin spinning processes and has been largely responsible for their supersession in favour of other methods of collecting wet cellulose filaments. In the modern cuprammonium process an arrangement is used like that in G.P. 432285 of 1925, whereby the yarn is spun on to swifts of normal hank girth, which are collapsible, and from which the yarn is removed in the form of hanks for washing and drying. This procedure, wherein the yarn receives no twist, is practicable only because the filaments in each yarn adhere together, although they will separate on subsequent handling. If the filaments were entirely free from one another the yarns would become hopelessly entangled and impossible to wind in the absence of any twist.

When cuprammonium rayon is spun on to swifts, these must be removed from the spinning machine at intervals and the individual hanks from each spinneret must be laced with three or four tie bands. The swifts can then be collapsed and the hanks removed. They are processed by similar methods to those which were usual in the viscose industry until recently. The processing consists in hanging groups of hanks on to rods which are conveyed under a series of sprays to wash and finish the yarn. Normally the yarns are first washed free from acid with water and afterwards with soap or other softening agent. The yarn is finally dried and conditioned.

In England only one company, British Bemberg, is at present operating the cuprammonium process. Their yarns range in denier from about 35 up to about 180, although the filaments all have the same fine denier of 1·3.

Owing to the intense price competition between the different processes waste of any kind has to be avoided. In the cuprammonium process this entails recovering the copper from the acid wash-liquors.

Viscose Process.—The viscose reaction which produces a water soluble xanthate of cellulose was discovered by Cross, Bevan and Beadle (B.P. 8700, 1892). But attempts to spin satisfactory filaments from solutions of cellulose revealed a succession of difficulties, and it was many years before the process emerged from the experimental stage. According to Hard (*op. cit.*) the process was first commercially established in France, for although the earliest works had been started in England it was not until 1912 that it was firmly established here.

Wood pulp is the cellulose raw-material most used. It should have a low resin and ash content and a high content of α-cellulose (*v.* Vol. II, 460*c*, 465*b*). The pulp sheets should be soft and free from hard lumps. Taken over a period of years there has been a tendency for pulps of higher and higher α-cellulose-contents to be used in the industry. Now according to Hebbs (J. Soc. Dyers and Col. 1939, **55**, 550) the average value for rayon pulps is 89·5% α-cellulose.

Cellulose wood pulp is not a homogeneous product but consists of a mixture of celluloses with different degrees of polymerisation (Schieber, Papierfabr. 1939, **37**, 245). The least polymerised or most degraded ones are the so-called hemi-celluloses which are alkali-soluble. These are to some extent leached out in the mercerising process, and contaminate the mercerising lye, and are consequently undesirable. Highly polymerised celluloses give rise to very viscous viscoses which are difficult to handle and for this reason are also undesirable in the normal process. On the other hand Mark has shown theoretically that more highly polymerised (*i.e.* longer) molecules are more easily aligned by stretching than are less highly polymerised ones (Trans. Faraday Soc. 1933, **29**, 6). For this reason in spinning highly oriented viscose rayons by the Lilienfeld process (B.P. 274521) it was found that it was advisable to eliminate altogether the ageing process. The resultant viscose, though more dilute in cellulose than usual, was still very viscous and presented special problems in transport.

The sheets of pulp are mercerised in mercerising-strength caustic soda, usually about 18%, at about 20°C., for 1–2 hours under conditions which will ensure uniform penetration of the pulp (*v.* Vol. II, 465*b*).

The swollen sheets are next submitted to pressure at about 200 lb. per sq. in. to remove excess lye and to yield an alkali cellulose containing 28–30% cellulose and 15–15·5% sodium hydroxide. Both the mercerising and pressing are often carried out in a mercerising press of the kind shown in B.P. 7893, 1912.

The sheets of pressed alkali cellulose are now disintegrated in a machine with revolving arms such as that described in G.P. 400378 Cl. 29a. The disintegration is carried on for 2–3 hours until the alkali-cellulose now in the form of " crumbs " occupies about a litre for every 300–350 g.

The crumbs are emptied into sheet-steel vessels which are covered with lids and stored in a thermostatically controlled room for 2–3 days.

During this storage or " ageing " there is oxidation of the cellulose by the oxygen of the air enclosed in the porous mass of crumbs (Davidson, J. Text. Inst. 1932, **23**, T95). Consequent upon the oxidation there is a progressive fall in the viscosity of the viscose made from the aged crumbs, the relation of time and viscosity being approximately hyperbolic. According to Schieber (*l.c.*) this is because the more highly polymerised cellulose components only are broken down into shorter-chain celluloses, but Lachs, Kronman and Wajs (Kolloid-Z. 1938, **84**, 199) consider the order of heterogeneity remains the same although the mean chain length is decreased.

The presence of iron, copper and nickel accelerates the oxidation of cellulose in the presence of alkali (Davidson, *l.c.*) and although Lottermoser and Wultsch (Kolloid-Z. 1938, **83**, 180) confirm this effect on the ageing for traces of iron, they find copper has no influence. A rise in the ageing temperature produces more rapid oxidation of the alkali cellulose.

The xanthation or churning whereby the alkali-cellulose crumbs are converted into cellulose xanthate is carried out in rotating churns in a thermostatically-controlled room at between 20 and 25°C. The crumbs are placed in the churn which is closed and set rotating slowly whilst the predetermined quantity of carbon disulphide is introduced through a hollow trunnion. The reaction is exothermic and there is usually a temperature rise of 5–8°C. At first there is a rise of pressure in the churn due to the rise of temperature. After this the pressure falls, at first slowly and then rapidly as the carbon disulphide reacts. At the same time the colour of the mass changes from a creamy white to a yellow and then to an orange at which stage the reaction is stopped by evacuating the excess of CS_2 from the churn and subsequently emptying the contents into the dissolver. The usual reaction time is 3–4 hours.

According to Lieser (Micheel, " Chemie de Zucker u. Polysaccharide " Akad. Verlag, 1939) it is the hydroxyls attached to the C2 atoms of the glucose residues which react. The usual proportion of carbon disulphide is 32% on the weight of the cellulose which is theoretically sufficient to xanthate every glucose residue, but only one in two of the glucose residues is xanthated. The proportion is statistical since about half the cellulose chains are not xanthated (Lieser, Annalen, 1930, **483**, 132). An explanation based on the accessibility of the cellulose has been put forward by Lieser-Hall (Papier-Fabr. 1938, **36**, 272) and Schramek (*ibid.* 1938, **36**, 226) who suggest that the reaction may be intermicellar.

The cellulose xanthate is dissolved in dilute caustic soda by mechanical agitation to give a solution containing usually about 8·5% cellulose and 6·5% sodium hydroxide. The viscose thus obtained is filtered, and ripened until ready for spinning.

Viscose solutions differ from cuprammonium solutions of cellulose and solutions of cellulose nitrate and acetate, in that the latter are reasonably stable when kept in closed vessels, whilst viscose is unstable. Under normal conditions of temperature there is spontaneous decomposition due to a combination of hydrolysis and saponification (Klauditz, *ibid.* 1939, **37**, 251), the sodium cellulose xanthate giving sodium carbonate, sodium thiocarbonate and cellulose. The reaction probably proceeds heterogeneously in such a way that there is a mixture of varying proportions of cellulose and dicellulose xanthate (Frenkel, Cellulosechem. 1928, **9**, 25), the latter decreasing and the former increasing as the decomposition or ripening proceeds. Only the commercially uneconomic method of refrigeration will retard this process, so that under normal works conditions viscose made on a given day must be spun on another given day. In fact the only alternative to continuous production would be to clean out all the pipelines and storage vessels whenever the process was to be halted. The compulsion of this was seen during the stay-in strikes in France in 1936 when " The silk workers at Lyons, who not only have occupied an artificial silk factory, but have kept part of it working . . . have now furnished . . . (an) explanation of their motives . . . because the viscose used in the manufacture . . . if allowed to lie idle, would solidify in the machines and do damage which would take at least 2 weeks to repair " (*Times*, September 18, 1936).

The necessity to ripen viscose in order to achieve satisfactory spinning was discovered at an early stage by Stearn (B.P. 2529, 1902; 7023, 1903), and the methods claimed to obviate this process have not been found satisfactory in practice.

Ripening can be measured in several ways, of which the most important are the amount of combined sulphur and the ease of coagulation. The latter is the more common in works practice and can be carried out by determining the number of c.c. of 10% ammonium chloride solution required to coagulate 20 g. of viscose (Hottenroth, Chem.-Ztg. 1915, **39**, 119). The older and riper the viscose the less ammonium chloride is required and the lower the ripeness number. Nowadays viscoses are being spun at ripeness figures above 10, since the less ripe the viscose the less is its contraction on drying. There is a difficulty in using unripe viscose, as this is liable to give " milky " filaments unless the various conditions are properly adjusted.

Ripening is done in steel vessels kept in a cellar at constant temperature. During the operation the opportunity is taken to filter the viscose by forcing it under about 4 atmospheres pressure through presses from one vessel to another. It is most important that all mineral particles and undissolved fibres that might block the holes in the spinnerets, be removed by filtration. To this end open filtering media like cotton wool and flannelette are better than hard closely woven filter cloths. One of the advantages of the former is that their rate of decay of filtering efficiency is slower than that of the latter (Hermans and Bredée, Rec. trav. chim. 1935, **54**, 680). Other conditions being equal one of the indications of good viscose is the absence of undissolved fibres, and therefore a batch with which the filter presses show a slow rate of decay.

During the last few hours of the ripening process, the vessels containing the viscose are placed under vacuum in order to remove air bubbles and dissolved gases which would interrupt the flow of viscose from the spinnerets and cause breakdown in the spinning. When the time has arrived for spinning, the viscose vessel is put under air pressure and the appropriate valves opened to connect it with the pipeline to the spinning room. The large bore pipe leading from the ripening room subdivides into smaller pipes leading to the individual spinning machines. These pipes run along both sides of each spinning machine and are tapped at short intervals to supply the spinning pumps, which deliver a flow of viscose to the spinnerets that within reasonable limits is independent of the back pressure. The early method of controlling the flow of viscose and through this the denier of the filaments was by means of the pressure applied to the viscose solution. This method was unsatisfactory since variations of viscosity or of spinneret hole size caused variations in the rate of flow and of the denier. The old method of control was superseded at the beginning of this century by the use of measuring pumps (B.P. 16605, 1903; 5766, 1905). The first pumps had single pistons only and the inevitable variation of delivery rate had to be smoothed by the use of a small air bottle on the delivery side of each pump. Later multiple piston pumps (B.P. 17876, 1907) and gear wheel pumps (B.P. 28320, 1912) were devised whereby more uniform rates of flow are obtained. The latter type of pump is simpler, but is more sensitive to variations of back pressure and wear than is the multiple-piston-type pump (Mortgat, "La Fabrication de la Soie Artificielle par le Procédé Viscose," Paris, 1930, p. 221 *et seq.*).

The viscose delivered by the measuring pump is forced through a candle filter, then through a short length of pipe (made of glass or of steel covered with lead) which connects with the spinneret. This arrangement with slight variations is universally adopted and together with the use of multiple-hole spinnerets was described in Topham's B.P. 23157, 1900.

The spinneret is made of a material which will withstand the action both of hot dilute acid and of dilute caustic soda. Obviously only a limited range of materials have sufficient chemical resistance for the purpose. Pure platinum and its alloys with gold, palladium alloys with gold, glass, porcelain and tantalum alone or inset with synthetic rubies have all been used at one time or another. In recent years tantalum has become the most popular spinneret material, largely on economic grounds.

The number of holes in the spinneret controls the number of filaments spun. In the case of continuous-filament yarns they range from 18 up to 120, whilst for staple-fibre spinning they range from 500 up to 2,000. The size of the hole, although it does not affect the denier, is decided by the filament denier that can be spun through it; with a given composition of coagulating bath, the finer the filament that is required the smaller must be the hole from which it is spun (Bronnert, B.P. 174961). The usual dimensions of spinneret holes are 0·08–0·10 mm. diameter.

It is important that the side walls of the holes have a high polish since this retards the accretion of foreign matter and prolongs the life of the spinneret. Also it is important that the holes are all of equal size since otherwise filaments of different deniers will be spun by the same spinneret.

The viscose as it emerges through the holes in the spinneret undergoes several changes concurrently: (1) coagulation with the formation of a "skin" begins even before the filaments have left the spinneret hole; (2) attenuation of the filaments sets in owing to the speed of collection of the filaments being greater than the velocity of the viscose solution through the holes in the spinneret, as Ost showed in spinning cuprammonium solutions (Z. angew. Chem. 1918, **31**, 141); (3) dehydration of the filaments starts because the osmotic pressure of the coagulating bath solution is greater than that of the viscose solution (Lottermoser and Schiel. *ibid.* 1930, **43**, 80). The characteristic serrations of viscose cross-sections are due to 1 and 3, whilst the greater orientation of the "skin" is due to 1 and 2, together with the effect of streaming orientation (Preston, J.S.C.I. 1931, **50**, T199; Nature, 1931, **128**, 796; Lobering, Papier-Fabr. 1939, **37**, 9). An alternative explanation of the "skin" effect has been put forward by Sisson in a recent paper (J. Physical Chem. 1940, **44**, 513). He shows that the X-ray results agree with a tangential arrangement of the (101) planes of the cellulose crystallites in the "skin" due to the radial shrinkage of the filaments.

The exact stage during coagulation at which stretching or drafting will produce the best effect in orienting the cellulose crystallites in the filaments is important. If the drafting occurs in the spinneret whilst the interior of the filaments is not coagulated, only the skin will be oriented, on the other hand if the filaments are dehydrated too much there will not be sufficient freedom for the crystallites to align themselves without a partial breakdown of the structure (Hermans and collaborators, Kolloid-Z. 1937, **81**, 143, 300; 1938, **82**, 58; 1938, **83**, 71). The optimum condition for the application of draft lies between the two extremes and is conveniently carried out in practice when the filaments as they leave the coagulating bath are stretched between two godet wheels, the second of which is run at a higher peripheral speed than the first (B.P. 388344; 424824; 481777). Increasing the draft increases the strength of the filaments but decreases their extensibility (Tomonari, J. Cellulose Inst. Tokyo, 1937, **13**, 23).

Many of the early difficulties of the viscose process were connected with the coagulation of the filaments and various improvements were suggested as the process developed. B.P. 17503 of 1902 claims that viscose filaments which have been coagulated with acid and as a consequence contain precipitated sulphur, may be desulphurised with a sodium sulphide solution to produce colourless and lustrous rayon. However, acid alone is not satisfactory since the decomposition is too rapid and gives weak filaments containing hollow spaces (Bredée, Chem. Weekblad, 1933, **30**, 51). For this reason double baths were used, the first a salt bath to coagulate the viscose and the second an acid bath to decompose the xanthate and to regenerate cellulose. With gradually increasing knowledge it became possible to compound a bath satisfactorily combining coagulation and decomposition. The first to do this was Müller (B.P. 10094, 1906) who proposed to use a bath containing a high concentration of sodium sulphate together with sulphuric acid. Low concentrations of sodium sulphate have little effect, but when the relative concentration of sodium sulphate to sulphuric acid approaches 1 : 1 there is a rapid improvement in the strength of the filaments produced, with increasing sodium sulphate concentration (Bredée, *l.c.*) Although Müller's invention was a marked advance, the coagulating power of sodium sulphate alone is scarcely sufficient to harden the filaments so that they will not adhere together when they are pressed in contact at the guides and on the collecting device. Consequently yarns spun in this bath are liable to be hard and wiry. Cross-sections of filaments coagulated in this bath, when the filaments have had sufficient time to harden before coming into contact, are round to oval in shape and lack the marked serrations characteristic of modern viscose rayons spun in baths of greater coagulating power (Bunger, Doud and Sugarman, State Eng. Exper. Sta. Bull. Georgia, 1938, **1**, 21; Jäger, Kunstseide, 1931, **13**, 325; Bronnert, J. Soc. Dyers and Col. 1922, **38**, 153). In spinning, the ripeness of the viscose, the composition and temperature of the coagulating bath, the denier of the filaments, and the time of contact of the filaments with the bath are interrelated with one another and with the tensile properties of the spun filaments. Scherer and Hussey have shown that there is an optimum set of these conditions in spinning experiments using the Müller bath (Ind. Eng. Chem. 1930, **22**, 594; 1931, **23**, 297). When the filaments have come into contact before they have been sufficiently hardened their cross-sections have a polygonal shape.

Very full data for the solubility of sodium sulphate in the system $H_2O—H_2SO_4—Na_2SO_4$ at temperatures between 0° and 82·5°C. are given by Faust and Esselmann (Z. anorg. Chem. 1926, **157**, 290).

Müller mentions the use of zinc sulphate, but the greatly enhanced coagulating power of a bath containing an alkali sulphate plus a small amount of zinc sulphate was first expressed in the composition claimed by Courtauld and Napper (B.P. 406, 1911). The exact concentration of zinc sulphate is very important since Poznanski (Rayon Text. Monthly, 1939, **20**, 501) has shown that the rate of decomposition of viscose is decreased by increased zinc concentration. This explains why Tomonari (*l.c.*) found that increasing the zinc concentration decreased the spinning tension. Thus concentrations of zinc sulphate above about 2% produce so impermeable a skin on the filaments that under normal conditions the xanthate in the interiors of the filaments is incompletely decomposed by the acid in the bath. However, if the spinning conditions are suitably arranged so that decomposition is finally completed, then the coagulated but temporarily undecomposed filaments are in a condition suitable for stretching to give improved orientation (B.P. 467500). The Lilienfeld process (B.P. 274521; 274690; 281351; 317608) utilised the plasticising properties of concentrated mineral acids used as coagulating baths to enable filaments to be highly oriented by stretching, during spinning. A spinning machine such as described in B.P. 297618 or 317912 is necessary in order to prevent damage to the filaments from lengthy contact with the concentrated acid. The process was worked in England, 1926–30.

In coagulating baths containing about 1% zinc sulphate plus different concentrations of sodium sulphate the deviation of the cross-sections of the filaments from circularity, which is best measured by Hase's coefficient (J. Soc. Chem. Ind. Japan, 1932, **35**, 367B), is greater the higher the concentration of sodium sulphate (Bunger, *l.c.*). The deviation from circularity of the filaments spun in a given bath is practically independent of the denier (Okajima, J. Cellulose Inst. Tokyo, 1935, **11**, 39).

Magnesium sulphate when used together with an alkali sulphate behaves similarly to zinc sulphate in increasing the coagulating power and producing filaments with serrated cross-sections, however a higher concentration of magnesium than of zinc must be used (Verhave, B.P. 2485, 1915).

In the course of time there has been a tendency to spin less and less ripe viscose, in order to improve the quality of the yarn produced. This has demanded baths of increased coagulating power, such as the use of a mixture of sodium sulphate, magnesium sulphate and zinc sulphate (Bergen, B.P. 216125).

With a given filament denier and coagulating bath a certain time is required for complete decomposition of the viscose. At a constant rate of spinning this time will be proportional to the length of immersion in the bath and it has been found that the length of immersion required is inversely proportional to the diameters of the filaments (Inoue, J. Soc. Chem. Ind. Japan, 1939, **42**, 18B).

At one time many works used to collect the coagulated rayon yarn on bobbins, but largely because of the difficulties of drying the yarn on the bobbins and the need for subsequent twisting, this method has been discarded in favour of the centrifugal pot method, which was invented by Topham (B.P. 23157, 1900). In this method the yarn as it leaves the godet wheel is allowed to fall vertically into a funnel mounted on an arm which holds it on the axis of the pot. The pot, which has the form of a truncated cone of very small angle, rotates at a speed of 6–7,000 r.p.m. about a vertical axis.

The centrifugal force pulls the yarn through the tip of the funnel and throws it against the inner wall of the pot, where it gradually builds inwards a cylindrical layer of yarn. In order that the yarn shall be evenly distributed vertically and that the " cake " of yarn which is formed shall have reasonable mechanical strength, the funnel is given a reciprocating motion along the axis of the pot, with a constant velocity and as nearly as possible instantaneous reversal at the end of each traverse.

Rotation of the spinning pot not only collects the yarn but also twists it. This imposes a limitation, since a twist of about 2½ turns per in. is usually required, and as the spinning pot cannot be run economically at much higher speeds than those given above, the yarn speed cannot be greater than about 60–70 metres per minute. This limitation applies neither to bobbin spinning nor to staple fibre spinning since in neither case is the yarn twisted whilst it is spun. In these cases the limitation lies solely in the necessity for a sufficient time of contact between the coagulating bath and the filaments for them to be completely coagulated. Speeds of 100–200 metres per minute are practicable.

Until quite recently the next operation after the cakes had been spun was to reel these into hanks and then to wash, desulphurise and bleach the yarn in hank form. This is still done to some extent but not universally as formerly. The method which is coming into general use is to give the wet treatments to the yarn in cake form and then to dry and sell the yarn still in cakes. There are several reasons for the change. One is that the yarn in hank form, containing as it does only about 2½ turns twist per in., is very liable to entanglements and mechanical damage. This is avoided when the processing is done in cake form. Another reason is that processing in cake form can be more highly mechanised and consequently lower labour charges are incurred. Against this must be set the high capital cost of a satisfactory cake-treatment plant, and the fact that only perfect and perfectly uniform cakes can be processed on such a plant.

The principle of a cake-treatment plant is that the cakes are arranged in symmetrical groups with the bottom of one cake pressed against the top of the next, and arrangements are made to seal the ends of each group by plates which compress the group of cakes and thus seal the joints between contiguous cakes. The various wash liquors are now forced through an aperture in one of the plates into the interior cavity formed by the hollow centres of the group of cakes. The wash liquors then gradually percolate through the interstices of the cakes and are exuded from the outside. During this washing out of the cakes, filaments of the yarns receive a uniform and thorough extraction (B.P. 361733; 483856; 497239).

The wash liquors which are used successively are:

(1) Water to remove acid and other constituents of the coagulating bath.
(2) Sodium sulphide or sulphite solution to desulphurise the filaments.
(3) Water to remove the desulphurising wash.
(4) Acid to neutralise alkalinity.
(5) Water to remove acid wash.
(6) A soap or other water-soluble softening agent.

A bleaching treatment with hypochlorite or peroxide may be interposed between 3 and 4.

After the softening treatment as much water as possible is removed by hydroextraction and the cakes are then dried and conditioned to 10% moisture content. Drying requires more than a week and is a critical operation, for if it is hurried the outsides of the cakes will dry before the insides, they will attempt to contract against the resistance of the swollen inner layers and will consequently be strained (B.P. 358847).

Viscose and regenerated cellulose rayons in general show a much higher moisture adsorption at all relative humidities than do native cellulose fibres (Obermiller, Textilber. 1926, **6**, 765; Z. angew. Chem. 1926, **39**, 46; Urquart and Eckersall, J. Text. Inst. 1932, **23**, 163). The rayons also show a much greater volume-swelling in water than do the native cellulose fibres (Preston, " Modern Textile Microscopy," London, 1933, p. 40; Morton, Trans. Faraday Soc. 1935, **31**, 262; Hermans and de Leeuw, Kolloid-Z. 1937, **81**, 300). The increase in volume is about 100%, over 90% of which is transverse swelling, only about 5% being lengthways swelling. The dimensional changes that occur in the first drying of the newly spun material are still greater (Hermans and de Leeuw, *l.c.*) and are responsible for the difficulties in drying regenerated cellulose rayons.

The large volume swelling occurring on wetting dry viscose and cuprammonium rayons has been turned to good use in producing crêpe fabrics. Yarns with a twist of about 50–60 turns per in. are woven into fabrics which are subsequently wetted whilst they are free from tension. The wet filaments have a diameter about 40% greater than in the dry state and the stresses set up by this in the tightly twisted yarn can only be relieved by untwisting of the filaments or by contraction and the formation of snarls in the yarn. Since the yarn cannot untwist because of the weave, only the last can operate to relieve the stresses and they result in a shrunk fabric with a " pebble " effect on the surface. In this connection it is interesting to note that such a fabric extends in the direction of the crêpe yarn, when it is dried, because of the decrease in the diameter of the filaments, but the " pebble " effect remains.

It is a matter of considerable theoretical and practical importance that although the total volume swelling remains approximately constant, the lengthways swelling is inversely proportional to the orientation of the filaments produced by stretching during spinning. Commercial cellulose rayons have lengthways swellings varying from 1 to 8%. A measurement of this property is the simplest method of estimating the amount of stretching the rayon has had during spinning.

Cellulose Acetate Process.—The discovery of cellulose acetate is ascribed to Schützenberger (Compt. rend. 1865, **61**, 485), but under the conditions he used it is probable that the acetate produced was that of a degradation product of cellulose. Schützenberger later worked with Naudin on the same problem and although there is no indication that they tried to spin fibres, it is interesting that Naudin later became the manager of the first successful viscose rayon factory, the Société Française de la Viscose (Cross, *Manchester Guardian*, March 5, 1925).

The problem of producing cellulose acetate lies mainly in the difficulty of carrying out the necessary reactions without excessive degradation of the cellulose. This is inherent in the fact that acetic anhydride and acetic acid, the usual acetylating agents, have a very small swelling action on cellulose and therefore the reaction proceeds with great difficulty in the interior of the cellulose fibres. This difficulty must be obviated in some way. Three methods are possible: the fibres can be swollen in some suitable agent, and the swelling agent then displaced with acetic acid (Olsen, Ind. Eng. Chem. 1938, **30**, 524); the cellulose of the fibres can be degraded either before or during acetylation, thereby making it more readily dispersed; the fibres can be pre-treated in such a manner that, although dry when they enter the acetylation mixture, they are more easily penetrated by this mixture.

In practice a combination of the second and the third methods are used. That is the cellulose (usually cotton linters) is pre-treated so as to give it as open and easily penetrated a structure as possible and acetylation is carried out in the presence of a catalyst. The catalysts used bring about a depolymerisation of the cellulose, but they also have a solvent or swelling action on the cellulose and thus render it more reactive. Franchimont (Ber. 1879, **12**, 1941) was the first to suggest the use of a catalyst, but Cross and Bevan's was the first commercial process (B.P. 9676, 1894). This and other later patents on cellulose acetate granted to Cross, Weber and Frankenburg were acquired by Prince Guido Henckel von Donnersmarck, who had also financed the early experimental production of viscose. His factory in Germany subsequently produced the first experimental acetate rayon in 1902 according to Mork, Little and Walker's process (U.S.P. 712200, 792149).

The early processes all produced or envisaged the use of fully acetylated cellulose, and an important improvement was the partial hydrolysis of this to produce a cellulose acetate soluble in acetone, first suggested by Miles in 1903 (U.S.P. 733729; 838350; B.P. 19330, 1905). Although in the conversion of the chloroform-soluble triacetate into the acetone-soluble form some hydrolysis occurs usually, this appears to be a secondary effect. Thus whilst cellulose triacetate has a theoretical content of 62·5% acetyl expressed as acetic acid, acetone-soluble cellulose acetates can range from 51·5% to at least 60·0% acetyl, *i.e.* nearly completely acetylated cellulose can be acetone-soluble. In regard to this there has been an interesting observation by Taniguchi and Sakurada (J. Soc. Chem. Ind. Japan, 1938, **41**, 72B) that cellulose triacetate is completely soluble in acetone if intimately mixed with an acetone-soluble cellulose acetate. When this observation is taken in conjunction with Deripasko and Drujan's statement that a cellulose acetate of 54·7% acetyl content can be resolved into fractions ranging from 53·8 to 58·5% acetyl (J. Phys. Chem. Russ., 1937, **10**, 798), it suggests that acetone-solubility may depend on the presence of a particular constituent rather than on the average acetyl content (*v.* Vol. II, 464*d*).

The chief differences between acetone-soluble cellulose acetates of different acetyl content is that the more highly acetylated ones are more stable—they have higher softening points and are more difficult to delustre by hot aqueous treatments such as are described in B.P. 165164 and 358574. In fact above 60% acetyl content there is no delustring by the former of these processes and only slight delustring by the latter one, but in B.P. 478937 a slightly lower value of 56–59% acetyl is claimed to resist delustring. A slight variation is understandable, since the exact limit must depend on the conditions of delustring and the criterion of lustre.

The use of high acetyl-content cellulose-acetate yarns will be valuable when they are required to withstand hot aqueous treatments without delustring, for normal cellulose-acetate rayon cannot be treated wet above 85°C. without loss of lustre.

The moisture adsorption of cellulose is mainly a function of the hydroxyl groups present, so that it would be expected that the more complete the acetylation, the greater would be the reduction in the moisture adsorption. This expectation is confirmed by data published by Kanamaru and Chao (Kolloid-Z. 1938, **84**, 85) some of which are given below.

Relative humidity.	Moisture adsorption by		
	Viscose rayon.	Cellulose diacetate.	Cellulose triacetate.
%	%	%	%
90	28·86	10·98	6·71
60	15·5	5·7	3·8

The values for the triacetate, although low, are much higher than would have been expected from analogy with cellobiose octa-acetate and glucose penta-acetate, which absorb less than 1% moisture at saturation. Sheppard considers that the moisture in cellulose triacetate is held in discontinuities or intermicellar spaces in the structure (Trans. Faraday Soc. 1933, **29**, 77).

Cellulose-acetate rayons swell to only a very slight extent in water, since very little is adsorbed, and to this property must be ascribed the difficulty of producing a "pebble" by ordinary wet treatments in fabrics made from crêpe-twisted cellulose-acetate yarns.

Acetylation is carried out in practice by adding gradually 80 kg. of cotton linters (2–3% moisture content) to the acetylation mixture, previously cooled to 5°C., which consists of 195 kg. acetic anhydride, 325 kg. acetic acid and 10 kg. sulphuric acid as catalyst (Lipscomb, "Cellulose Acetate," E. Benn, London, 1933). The sulphuric acid swells the cellulose and reacts with it forming a cellulose sulphate, but is later replaced by acetic acid (Coltof, Amer. Chem. Abstr. 1935, 1634). The reaction is exothermic and there is a temperature rise of about 1°C. per 15 minutes for the first 2 hours, after which the reaction becomes more vigorous and the temperature rise must be controlled so that it does not exceed 2–2·5°C. per 15 minutes. After a further 2 hours the temperature should have risen to a maximum which should not exceed 35°C. During the rest of the process the temperature should fall slowly and after 1½ hours samples should be taken to ascertain that no unacetylated fibres are left. This examination is repeated until a perfectly clear solution is found (Lipscomb, *op. cit.*, p. 54).

The cellulose acetate must now be converted into the acetone-soluble form by "ripening," which is done by adding 18 litres of water to the acetylation mixture described above and storing it at a temperature of about 21°C for 65–75 hours. Towards the end samples are withdrawn, the cellulose acetate precipitated with water and tested to ascertain its ripeness. It is sufficiently ripe when it will not dissolve but becomes plastic in warm chloroform, also it should dissolve in 5 c.c. of a hot mixture of equal volumes of benzene and alcohol to which not more than 2–3 drops of water need be added. The cellulose acetate is now precipitated (after neutralising the sulphuric acid with 17 kg. of sodium acetate) by the addition of 400 litres of water. The cellulose acetate is drained, centrifuged and washed with water (Lipscomb, *op. cit.*).

The acetate must now be stabilised to remove traces of sulphuric acid esters which otherwise would bring about hydrolysis in the presence of water (Rogovin and Ioffe Org. Chem. Ind. U.S.S.R. 1937, **4**, 425). This is usually effected by boiling with 0·02% sulphuric acid for 1–2 hours (Jeanny, Rev. Gen. Mat. Plast., 1938, **14**, 7). After this the cellulose acetate is washed, hydroextracted and dried. It can then be used immediately or stored.

The solution for spinning is prepared by dissolving the cellulose acetate in a mixture of 95% acetone and 5% water to obtain a concentration of 20–25%. The solution must be more carefully filtered than in any other rayon process because the spinneret holes used are smaller in acetate spinning than in the other processes. Filtration is carried out in the same manner as with viscose except that somewhat higher pressures are needed. The filtering materials used are cotton wool, and closely woven cotton and silk fabrics. The solution may also be filtered through metallic wool to remove traces of sulphur compounds (B.P. 465028), which otherwise are liable to react with the spinneret metal and block the holes with incrustations of metallic sulphides.

Cellulose acetate solutions are usually spun by evaporative processes, although a large number of wet spinning processes have been patented. The usual type of spinning machine in England appears to be of the type described in B.P. 165519 and 198023. These patents were granted to the British Cellulose and Chemical Manufacturing Company, now the British Celanese Company. An important patent action was started in 1933 and was finally decided by the House of Lords in 1934, who held that the patents were invalid (*Times*, February 11, 1934).

Celanese began the commercial production of cellulose acetate rayon in 1920, following on the parent company's production of large quantities of cellulose acetate dope for military use during the war (1914–18). Subsequently Celanese, Ltd., Courtaulds, Ltd. and Lansil, Ltd., have been producing cellulose-acetate rayon yarns in England.

Spinning is done by supplying the cellulose acetate solution under about 6 atmsospheres pressure by pipelines to the spinning machines. The supply pipes are carried to the tops of the machines and are tapped at intervals to connect with the measuring pumps and final filters similarly to viscose spinning. The spinnerets are connected immediately below the filters and are directed downwards. They are made of a non-corrosive base metal alloy such as monel metal. They are of larger diameter than is used in viscose spinning and are drilled with only a single circle of holes, the sizes of which range from 0·05 to 0·07 mm. diameter for filaments from 1 to 5 deniers.

The spinning is started by wiping the face of the spinneret with a cloth damped with acetone, when, if the operation is carried out skilfully, the filaments fall freely from the spinneret. As they fall they meet an ascending column of dry air at a temperature of 48–58°C. (B.P. 407024) in the tall rectangular spinning chamber. As the filaments descend the acetone is progressively evaporated and carried away in the air which is withdrawn through apertures at the top of each chamber and taken through ducts to the acetone-recovery plant. When the filaments reach the bottom of the chamber which may be 12 or more feet high depending on the speed of spinning, the filaments have lost most of their acetone content and are sufficiently hard not to adhere when they come in contact with one another. They are then collected together and led through an aperture in the front of the chamber, over a lubricating device and then round a cylindrical steel godet cylinder which controls the spinning speed. From the godet they are carried to a cap-spinning device which simultaneously twists and collects the twisted yarn on a bobbin.

Since acetate rayon requires no wet treatments after spinning, it is not necessary to give it such a high twist as is required for viscose rayon, thus although the cap spindle does not run at more than about 10,000 r.p.m., it is possible to spin at more than 200 metres per minute. Cellulose-acetate rayon requires no further treatment and is ready for immediate use in any normal textile operation.

Processes have been described for improving the strength of cellulose-acetate filaments, by stretching them (B.P. 465601; 469749), such yarns have about 5 times the strength, but only a third of the extensibility of normal acetate yarns (Textile World, 1939, **89**, No. 9, p. 80).

Highly stretched cellulose-acetate rayon yarns can be saponified, to produce highly oriented cellulose-rayon yarns. Saponification is best carried out with an organic amine such as ethylenediamine, since the conversion is then done without loss of strength (B.P. 417220; 429103). It is understood that the Celanese strong yarn MV is produced in this way. This yarn has a small residual content of acetyl groups and swells to a less extent in cellulose swelling agents than do other cellulose rayons. Possibly because of its small swelling in aqueous solutions it has a low affinity for direct dyestuffs. However, the dye affinity can be improved by pre-treatment with dilute caustic soda solution (B.P. 501768).

Since most of the hydroxy groups in cellulose have been converted into ester groups in cellulose acetate, it is perhaps not surprising that the dyestuffs which had been devised for cellulose and protein fibres were useless for acetate rayon. Thus in 1920 when the problem of producing satisfactory acetate rayon had been solved, there still remained the problem of dyeing it. The first solution was not in fact a solution at all but merely a way of meeting the difficulty. It was done by regenerating a " skin " of cellulose (Preston, Rayon Record, 1930, 4, 651) on the surface of the filaments, by partially saponifying them with a hot dilute alkali solution (B.P. 20672, 1920; 169741). Partial saponification enables acetate rayon to be dyed with any cellulose dyestuff, but 10–30% saponification is required, which of necessity entails a considerable loss of weight and some loss of strength. The method is now used principally for obtaining good whites in discharge prints. A large range of special acetate-rayon dyestuffs have since been developed.

Green and Saunders of British Dyes brought out the first special acetate dyestuffs, the *Ionamines*, in 1922 (B.P. 197809). This invention was followed by others in which water-insoluble dyestuffs were dispersed with emulsifying agents like sulphonated ricinoleic acid, the initial letters of which, S.R.A., have been used as the name for one group of these dyestuffs brought out by Ellis and the British Celanese Company in 1923 (B.P. 219349). The "*Duranol*" colours, which were also dispersed insoluble dyestuffs, were brought out by B.D.C. in 1923. These dyestuffs lacked the water-solubilising groups (*e.g.* sulphonic acid groups) which are present in water-soluble dyestuffs and which were believed to prevent dyeing on cellulose acetate.

Kartaschoff (Helv. Chim. Act. 1925, **8**, 928) has shown that the dyeing of acetate rayon with dispersed dyestuffs consists first in an aggregation of dyestuff particles on the fibre surface followed by the solid solution of the particles in the fibres. Recently a new class of acetate dyestuffs has appeared which have their hydrophilic groups at the ends of side chains attached to the dyestuff molecules (B.P. 435807; 437516; 437745; 431514) (*v.* ACETATE SILK DYES, Vol. I, 39, and DYEING, Vol. IV, 137).

Alginate Fibres.—Alginic acid (*q.v.*) is a linear high polymer closely related to cellulose in constitution. The chief difference between them is that the primary alcohol group of each C6 atom in cellulose is replaced by a carboxylic acid group in alginic acid (Hirst and collaborators, J.C.S. 1939, 1880). Like cellulose, alginic acid can be formed into fibres, but the intrinsic difficulties of forming fibres from these two substances are reversed. With cellulose the difficulty is to disperse it in a liquid state before extrusion, whilst with alginic acid the difficulty is to prevent the spun fibres from dispersing in alkaline solutions.

Sodium carbonate or hydroxide solutions will disperse alginic acid with the production of viscous solutions which can be spun into fibres by extrusion into dilute sulphuric acid (Kringstad and Lunde, Kolloid-Z. 1938, **83**, 202). Fibres of the free acid are unsatisfactory since they are so easily dispersed, however some improvement can be made by converting the acid fibres into calcium alginate fibres by a treatment with calcium chloride solution (B.P. 415042; 492264).

Calcium and aluminium alginate fibres show excellent anti-crease properties and, in addition, because of their high mineral content, are non-inflammable. They behave on ignition similarly to weighted silk. The strength of these fibres is not as good as that of first quality viscose and they show a similar loss of strength on wetting. Calcium, aluminium and some other metallic alginates although insoluble in water suffer from the disadvantage that they will not stand alkaline washing, due to base exchange taking place with the formation of the soluble sodium alginate; chromium alginate, however, appears to be free from this disadvantage.

Alginic acid is prepared from kelp by alkaline extraction and is an article of commerce since it has other uses besides that mentioned here. It can be obtained in the pure form under the name of "*Manucol*" from Albright and Wilson, Ltd. Apart from the use of purified alginic acid, certain processes of Japanese origin indicate that it is not necessary to separate and purify the alginic acid before forming into fibres, but merely to disperse and spin various kinds of algæ (B.P. 417222; 420857; F.P. 826391). It seems unlikely that fibres formed in this way can be white and transparent without extensive after-treatment.

Alginate fibres have valuable potentialities in Britain as the raw material is available in large quantities on the Scottish coast. Furthermore the process of manufacture appears to be simpler than any so far proposed for other artificial fibres.

Synthetic Fibres.—It is only within the last few years that molecules of fibre-forming substances have been recognised as linear polymers of high molecular weight. Many problems of fibre structure remain unsolved but the general form of fibre molecules has been established by a great deal of experimental work. Much of this work, and in fact all of the earlier work, consisted of investigations of natural fibres and fibre-forming substances. The theory of the structure of the macromolecules of natural fibrous substances as linear polymers of high molecular weight was arrived at by a combination of chemical investigations of their degradation products and the application of the methods of X-ray crystallography to the fibres themselves. Other methods of investigation have played an important though subsidiary part.

In the last 13 years a number of attempts have been made to produce fibre-forming substances of synthetic linear polymers. One of the earliest attempts in this direction was the production of polyoxymethylenes by Staudinger, Johner, Signer, *et al.* (Z. physikal. Chem. 1927, **126**, 425). They were able to produce polymers estimated to contain more than 50 structural units and which although not capable of forming fibres in the textile sense, did give fibrous structures. This was an interesting achievement since it was a deliberate attempt to synthesise a fibre-forming substance, but the idea was not novel. Already in 1913 an isolated patent had been taken out claiming the production of fibres from solutions of polymerised vinyl ester (G.P. 281877, Cl. 39b).

Since the production of polyoxymethylene, Staudinger and his collaborators have produced many other linear polymers, for example polystyrene and polyacrylic acid. An account of this work up to 1932 is collected in Staudinger's "Die Hochmolekularen Organischen Verbindungen," Berlin, 1932. In addition numerous other papers by the same worker have appeared since that date.

Much valuable work on the synthesis and properties of linear polymers has been done in the laboratories of du Pont de Nemours and Co. in the United States and a large number of papers from these laboratories have appeared in the J. Amer. Chem. Soc. from 1929 onwards by Carothers and his collaborators.

In 1932 Carothers and Hill claimed to be the first to have produced "strong, pliable, transparent, permanently oriented fibres" which "simulate natural silk," from "strictly synthetic material" (J. Amer. Chem. Soc. 1932, **54**, 1579). In the same group of papers of which this is one, these authors describe the production of "superpolymers" which are defined as linear polymers having molecular weights above 10,000. They state that to obtain a useful degree of strength and pliability in a fibre requires a molecular weight of at least 12,000 and a molecular length of not less than 1,000A, although somewhat lower values would be valid for polyamides, probably because of their strong polar groups. The production of superpolyesters, mixed superpolyamides and superpolyesters, and superpolyanhydrides is described, and all these are stated to produce fibres of very satisfactory quality. In fact curves are given to show that superpolyesters yield fibres after stretching and orienting that rival silk in elasticity. Unfortunately superpolyesters suffer from the defects of low melting-points and considerable solubilities in organic solvents. Superpolyanhydrides have the defect of hydrolysing on standing in the atmosphere, so that superpolyamides and mixtures of these appear to be the only ones of these superpolymers free from defects (*ibid.* 1932, **54**, 1559, 1566, 1569, 1579).

Linear polymers are of two types. The first is formed from the monomer by simple addition. The second is produced from the monomer by the elimination of simple molecules (H_2O, HCl, $NaCl$, NH_3, etc.). In the latter type the molecular formula of the monomer differs from that of the structural unit of the polymer. This type might also be termed polyintermolecular condensation and requires at least two functional groups to be present in each monomer molecule, *e.g.* hydroxy acids might lead to polyesters and amino acids to polyamides. Whether or not a linear polymer of the second type will be formed depends on whether the reaction is intermolecular or intramolecular. If the latter a simple monomeric ring will be formed, but if the former either a polymeric ring or a polymeric chain will be formed. Structural and stereochemical factors will usually be of the most importance in deciding whether the reaction will be intermolecular or intramolecular. That is the reaction will be chiefly controlled by the nature of the reacting molecules and to a less extent by the conditions of the reaction. Generally if a 5- or 6-membered ring can be formed the reaction will be intramolecular, but if a 7- or higher-membered ring would result, then the reaction is intermolecular with the formation of a linear polymer (Carothers, *ibid.* 1929, **51**, 2548).

An X-ray study of the superpolyesters of the ethylene sebacate type shows that these possess a uniaxial form of crystallite orientation. Clear fibre patterns were obtained from which the calculated fibre period did not agree with the fibre spacing derived from the chemical formula on the basis of a planar model. This is ascribed to the attractive forces between the ester groups, and non-planar models are given which agree with the experimental results (Fuller and Erickson, *ibid.* 1937, **59**, 344). Examination of similar polyesters by Storks using an electron diffraction method confirms the fibre periods found by the X-ray method (*ibid.* 1938, **60**, 1753).

The molecular size distribution which has received some attention in the case of cellulose, as has been mentioned under viscose, has been investigated by Flory, who has given a theoretical discussion for superpolyesters (*ibid.* 1936, **58**, 1877).

Following on the extensive research work done in their laboratories, which has been briefly outlined above, du Pont de Nemours and Co. have protected the manufacture of synthetic superpolymer fibres by a series of patents from 1931 onwards. In U.S.P. 2071250 the superpolyethers, superpolyesters, superpolyamides, superpolyanhydrides and superpolyacetals, the molecular weights of which exceed 10,000 are claimed to give strong pliable fibres. These fibres give X-ray patterns indicating orientation parallel to the direction of stretching. The superpolymers are produced by heating the necessary reactants to a temperature of 150–300°C. in a molecular still at very low pressures. In addition detailed claims are made for a number of superpolyamides made either from ω-aminocarboxylic acids (B.P. 461236) or from diamines and dicarboxylic acids (B.P. 461237), or from previously formed salts of diamines and dicarboxylic acids (B.P. 474999), or from diamines and dicarboxylic acids one of which contains an O or S atom in the chain connecting the reactive groups (B.P. 487734). These are stated to give fibres either from melts or from solutions in solvents such as phenol. The process of polymerisation is facilitated by the addition of about 30% water which is removed in the final stages (B.P. 506125).

Probably for the reasons that Carothers and Hill mixed superpolyesters with superpolyamides a non-polymerising amide-forming substance can be added to the diamine-dicarboxylic acid mixture (B.P. 495790), and generally melting-point depressors of non-polymeric type may be added (B.P. 501527).

The cold-drawing reported by Carothers and Hill to give greatly improved properties to superpolymer fibres is claimed to be most effective when the fibres are wet (B.P. 491111) and a further improvement is effected if the superpolyamides after extrusion are first rapidly chilled before cold drawing (B.P. 501197). A variation of the final treatment of the fibres after extrusion in which the fibres are cold-drawn while wet with a mild swelling agent, and then crimped by mechanical means or by drying in a relaxed condition gives wool-like fibres that can be cut into suitable staple lengths (B.P. 514821). Treatment with steam can be used to set the form of the fibres (B.P. 504344). Synthetic superpolyamide fibres made by the above processes were put on the American market in December, 1939, under the name of "nylon" which du Pont de Nemours & Co. propose as a generic name and not a trade name. It is not clear from the statements available if the name is intended merely to describe superpolyamide fibres or whether it is to include all superpolymers. If the latter it would by Carothers's definition include cellulose and thus overlap the recent American definition of rayon given at the beginning of this article.

Nylon production in the United States is expected to be 4·6 million lb. in 1940 (Text. World, 1940, **90**, No. 1, p. 52). A description of the dyeing properties of nylon has been given by White (J. Soc. Dyers and Col. 1939, **55**, 409) (*v.* DYEING, Vol. IV, 126*a*).

Apart from nylon no other polymers of the intermolecular condensate type have been used for fibre production, but numerous polymers of the type produced by simple addition at double bonds have been proposed for making artificial fibres. An early patent on polyvinyl esters has already been referred to, but it was not until 1939 that polyvinyl fibres were produced commercially. In that year the I.G. Farbenindustrie exhibited-polyvinyl-chloride-fibre materials at the Leipzig Spring Fair, under the name of "*P.C. fibre,*" whilst in June, 1939, the Carbide and Carbon Chemicals Corp. began supplying a co-polymer of vinyl chloride and vinyl acetate under the name of "*Vinyon.*" The I.G. Farbenindustrie patents cover the addition of various substances to the polyvinyl chloride which may or may not be removed from the final product. Both thermoplastic extrusion and extrusion of a solution in some such solvent as methylene chloride are used (B.P. 473616; 496233; 508851).

The process of the Carbide and Carbon Chemicals Corp. (U.S.P. 2161766) uses a co-polymer of vinyl chloride and vinyl acetate containing 85–90% of the chloride. This is dispersed in acetone to give a dope containing 23% of co-polymer, which after filtering is dry spun by a process similar to that used for cellulose acetate. Though similar there are some differences between the processes. Thus the Vinyon filaments are collected on the bobbin without twist, where they are allowed to remain for some hours before being wet twisted on a duplex ring twister with 6 turns/in. The need for wetting during this and other subsequent processes is because of the low moisture content and consequent great electrical resistance and difficulty with static electrification. The twisted yarn is stretched about 140% to improve its strength and is then "set" by immersion in water for 2–3 hours at 65°C. (Text. World, 1939, **89**, No. 8, p. 54). The mechanism of vinyl polymerisations has been discussed by Flory (J. Amer. Chem. Soc. 1937, **59**, 241), and the structure by Marvel and Levesque (*ibid.* 1938, **60**, 280) and by many other workers.

Up to now polyamide and polyvinyl chloride fibres are the only synthetic fibres with satisfactory tensile properties that have been produced, but there is no reason to suppose that this state of affairs will persist. Apart from these two polymers many others have been used for making fibres with more or less success. Thus polyethylene (B.P. 472051; 511054) and polystyrene (B.P. 478333) have been protected as fibre-forming substances. Staudinger and Stanley have described the wet spinning of polystyrene fibres. Such fibres, although quite flexible at higher temperatures, are unfortunately brittle at normal room temperatures. They have the low strength and extensibility of only 0·72 g./den. and 6% respectively (Chem. and Ind. 1938, **57**, 14).

The properties of nylon, P.C. fibre and Vinyon are generally excellent, but there is one property in which they are inferior, even to cellulose acetate rayon and much more so to cellulose rayons and natural fibres, that is in respect of their moisture absorption. The reason is the complete absence of hydrophilic groups in some cases and in other cases the comparatively small number of these groups in the synthetic polymers in comparison with cellulose, fibroin and keratin. The importance of the hygroscopicity of wool fibres used in clothing has been indicated recently (Cassie, J. Text. Inst. 1940, **31**, T17) (*v.* FIBRES, ANIMAL. WOOL, this Vol., p. 107*c*).

CONTINUOUS PRODUCTION OF RAYON.

Nowadays rayon ready for immediate use is produced by the acetate process without any interruption between the extrusion of the filaments and the collection of the twisted yarn. Most other processes are discontinuous. The normal viscose and cuprammonium processes are carried out in a series of steps in which the yarn is extruded in the first step, washed in the second and dried in the third. The reason for the difference between the acetate process and the viscose and cuprammonium processes is obvious, after even a superficial consideration of the sequences of operations involved. The acetate process is entirely dry, whilst the viscose and cuprammonium processes require a sequence of wet treatments. Yet the fact remains that transparent films are made by continuous viscose and cuprammonium processes, so that there is no fundamental difficulty in the way of continuous-rayon yarn production by wet processes, provided a number of difficulties can be overcome. The chief of these is the necessity of giving a sufficient length of time for each wet treatment, and this necessitates the accommodation of some 30 metres of yarn in each wet process without occupying an excessive floor space.

The earliest attempt to wet-spin yarn continuously was Lehner's process (Swiss P. 4984, Cl. 19) which was devised in the last decade of the last century, for the wet-spinning, denitrating and twisting of rayon produced by a nitrate process. The twisting device used was an ordinary cotton type flyer frame.

In a later patent continuous production by either the viscose or cuprammonium processes was claimed to give improved yarns (B.P. 16495, 1907), drying being accelerated by first heating in the presence of steam (B.P. 20630, 1899) though it is not clear how the difficulty of the length of treatment was to be overcome. The first practical solution of this difficulty was proposed by Eck (G.P. 300254, Cl. 29a). In his machine the freshly spun yarn was carried round two sets of driven rollers arranged on two parallel axes one above the other. In its passage the yarn was displaced step-wise along these rollers whilst at the same time passing through the required sequence of baths. Finally the yarn was dried and collected. The arrangement was reasonably compact, but it may be surmised that it was a very difficult operation to lead the yarn round the rollers when starting the spinning. Another machine for the same purpose was described by Denis in 1920 (B.P. 125394), but Eck's machine was the more practical thought it does not appear to have been used on a commercial scale (*cf.* "Staple Fibres," *next column*).

The Furness machine, B.P. 378467, was a great advance on any of the earlier continuous spinning machines. It contained a mechanism for automatically displacing turns of yarn along a rotating cage and it appears to be the prototype of the machines which have found large-scale application and are described below.

Recently the Industrial Rayon Corporation of America have put into operation a satisfactory continuous-spinning process for viscose. Production is 240 million lb. a year and a saving of 1½*d.* per lb. is claimed. The total processing time from the extrusion to the dry twisting of the yarn instead of requiring several days is completed in 4½ minutes, (Jentgen, Kunstseide, 1939, **21**, 327, 374; Text. World, 1939, **89**, No. 10, p. 86). The difficulty of providing sufficient length of treatment in a compact space has been solved by a special form of bobbin consisting of two sets of interlaced bars. As the bobbin rotates the sets of bars move in relation to one another in such a way that the yarn wound round the bobbin is progressively displaced from one end of the bobbin to the other (B.P. 413413; 413414). In this way successive windings of yarn never overlap and about 70 turns of yarn are slowly travelling along each bobbin, being wound on at one end and led off at the other. The length of the bobbin is 7–8 in. and the diameter 5–6 in. so that there are about 100 ft. of yarn on each bobbin, and assuming the spinning speed to be normal, the yarn will be held on the bobbin for about 30 seconds. This is found to be sufficient for the successive wet treatments and for the final drying. The yarn travels downwards from bobbin to bobbin for each successive treatment and all the bobbins are compactly arranged and easily accessible. The yarn is finally twisted and collected on a cap-spinning device as in acetate spinning (B.P. 474973; 474974; 475023).

Staple Fibres.—Because of the preoccupation of the early rayon producers with the problem of making a substitute for silk it is not surprising that in the early days of the industry scant attention was given to the production of staple fibres. One of the difficulties was the economic one, that staple-fibre rayon would have to compete with wool and cotton and consequently would have to sell at a much lower price per lb. than continuous filament rayon which was in competition with silk only. Another difficulty was that, in the early days at least, rayon was used mainly for fabrics not subjected to hard wear whereas staple-fibre rayon as a cotton and wool substitute, would be expected to be much stronger. It was only when improvements in technique which minimised these difficulties combined with the necessity of Germany to replace imports of wool and cotton stopped by the blockade, that large-scale production of rayon staple-fibre began in Germany during the war (1914–18). The earliest rayon staple-fibre patent had been obtained a few years before 1914 by Pellerin who realised that production could be cheapened since uniformity was not of the same importance as in continuous-filament production (B.P. 7748, 1910).

Obviously any continuous-filament rayon can be converted into staple fibre by the mere act of cutting it into short lengths. In the early productions this method was used for viscose and cuprammonium staple-fibre although, unless it was a matter of disposing of waste rayon, much thicker strands of filaments were spun in staple-fibre processes so that a great number of fibres could be produced at each cut. These thick strands were produced by combining the bundles of filaments from a number of multi-hole spinnerets (B.P. 7562, 1913; 163312). This was the first step in the direction of cheapening the process by the introduction of mass production methods. The next step was obviously to convert the normal discontinuous viscose and cuprammonium processes into continuous processes. This has been discussed in relation to continuous filament rayon in the last section. The difficulties in respect of staple-fibre production are similar though not so great since breaking or damaging a small proportion of the filaments is unimportant. The earlier apparatus was similar to that used for continuous-filament rayon, that is the strand of filaments was washed, bleached and dried whilst passing round a series of drums (B.P. 286603; Fr.P. 625049). It was then cut into staple lengths. Produced in this way the fibres were too straight for satisfactory spinning on cotton or wool machinery, and methods have had to be devised to give the fibres a crimp or curl. During recent years many methods have been proposed for this purpose. One method was to run the fibres through a nip between pairs of fluted rollers before cutting them (B.P. 291120). The method adopted now is to cut the fibres at some stage during the wet processing and to allow the various liquid treatments (and the drying without tension) to distort the fibres and produce as much curliness as possible whilst they are carried along a travelling band. In addition various devices have been suggested in order to intensify this, such as stretching the filaments before cutting (B.P. 499671) or by cutting coagulated but not decomposed filaments (B.P. 509572) in order to increase their contraction after cutting. Numerous cutting machines have been devised, some of which include arrangements for crimping the fibres at the time of cutting (B.P. 498184; 501299; 504792; 507289; 507406; 508228; 511867).

Another way in which staple-fibre production has been improved is in using high speeds of spinning since the limitation imposed by the spinning pot or other twisting device used in continuous-filament production does not apply.

Electrical Spinning.—Except for the earliest processes mentioned all those that have been described so far have used spinning machines in which the fibre-forming substance has been extruded through spinnerets and collected by mechanical means. Up to now this has been the only method which has been successful commercially, but it is not the only method available. Another method is electrical spinning.

In 1900 Cooley described a method of forming filaments by extruding a stream of spinning solution (though the method should apply equally to a melt) into a high tension electric field, whereby the stream breaks up into filaments which harden by evaporation of the solvent and are later collected (B.P. 6385, 1900). Recently other electrical spinning processes have been described (U.S.P. 2048651; B.P. 492966; 514736). These processes are most suitable for use with non-aqueous solutions and it is possible that some such process may be used for large scale staple-fibre production if certain inherent difficulties can be overcome.

MODIFICATION OF PROPERTIES.

In the early days the high lustre of rayon was an advantage, but later it was found desirable to modify this in order to produce novelty yarns and yarns with a softer and more silk-like lustre. Other modifications also have become desirable for special purposes, such as modification of the dyeing properties or even of producing coloured yarns. These modifications have been achieved in practice by incorporating various solid and liquid substances in the spinning solution before extrusion. As far as the general spinning processes are concerned it is immaterial if these additions are dissolved or dispersed in the spinning solution, always provided in the latter alternative that the particles are sufficiently fine. The particle size usually found satisfactory lies in range 0·1–1·0μ.

The earliest modification proposed was that contained in Wagner's G.P. 137255 of 1901. In this it was proposed to add various iridescent fine powders to cellulose nitrate solutions before extrusion in order to produce opaque filaments.

Very many substances have been suggested as additions to spinning solutions in order to reduce the lustre of the spun filaments. Of these the most important have been petroleum jelly as an addition to viscose (Courtaulds, B.P. 273386) which gives a moderate reduction of lustre, and titanium dioxide (Singmaster, B.P. 339603; 342743) which may be added to any spinning solution and gives a perfectly mat or chalky appearance even if present to the extent of only about 3%.

More particularly in the case of staple fibre it has become necessary to confer the property of dyeing with acid dyestuffs upon cellulose rayons in order that these will dye a solid or approximately solid shade when admixed with wool. This has been carried out by adding various nitrogenous substances to viscose and cuprammonium solutions before spinning. Many substances such as natural proteins, and synthetic resins containing free amino-groups have been used (Fr.P. 840773; B.P. 501603; 501611; 509852).

Rayons containing pigments and dyestuffs are spun but the range of shades available is very limited.

GENERAL PROPERTIES OF RAYONS.

Fine Structure.—Rayons, in common with the natural fibres, consist of linear polymers of high molecular weight. They are long chain compounds in which the chain unit is repeated many hundreds of times. The textile qualities of the fibres are governed mainly by the character and arrangement of these chains. Considering the chains in more detail, the important factors are—(1) The chemical nature of the chain unit, which controls such properties as moisture adsorption, solubility and melting-point; (2) the number of units in the chain, often termed the degree of polymerisation or inversely the degree of degradation, which controls strength and flexibility and also modifies the solubility and melting-point; (3) the cross-links between the chains and the distance between the chains, which control the solubility, the extensibility and the elasticity (Mark, Nature, 1938, **142**, 937); (4) the arrangement (or orientation) of the chains in relation to one another, which has a marked influence on the tensile properties and the anisotropy (Hermans and collaborators, Kolloid-Z. 1937, **81**, 143, 300; 1938, **82**, 59; 1938, **83**, 71).

The effect of the chemical nature of the chain unit can be best seen by considering the different rayons. As a first example the difference between the properties of the hydroxyl groups of cellulose and the ester groups of cellulose acetate is reflected in the higher moisture adsorption of the former, and the fact that only the latter is soluble in organic solvents such as acetone, chloroform, methylene chloride and acetic acid. Again the different properties of the hydroxyl and acetyl groups in the degree of their associative forces are shown for instance in the fact that cellulose acetate will melt whereas cellulose will not. As other examples the amino- and imino-groups of casein and superpolyamide fibres (nylon) confer the ability to dye with acid dyestuffs, whilst the considerable proportion of hydrocarbon chain in the polyamide molecule gives it a very low moisture absorption and allows it to melt without decomposition. Similarly the absence of hydrophilic groups in polyvinyl chloride fibres (Vinyon, P. C. fibre) confers a negligible moisture absorption.

Irrespective of whether it is a matter of depolymerising a highly polymerised natural substance like cellulose or casein, or of polymerising a small molecule like styrene or vinyl chloride, the chain length or degree of polymerisation is a decisive factor firstly in deciding the possibility of fibre formation and secondly in influencing the properties of the fibres formed. In the case of polystyrene Staudinger (" Die Hochmolekularen organischen Verbindungen," Berlin, 1932, p. 186) states that a degree of polymerisation of 1,200 is needed before fibres can be produced from the polymer. Similarly with the polyesters of ω-hydroxydecanoic acid Carothers and Van Natta (J. Amer. Chem. Soc. 1933, **55**, 4714) state that only very short and weak fibres can be produced with a degree of polymerisation of 33, a degree of polymerisation of 100 being required for easy spinning of filaments with a fair strength (*cf.* Synthetic Fibres, p. 124*d*).

For obvious reasons most interest up till now has centred round cellulose, and this shows relations between the degree of polymerisation on the one hand and spinnability and strength on the other similar to those of the synthetic polymers. According to Staudinger and Reinecke (Kunstseide, 1939, **20**, 281) with a degree of polymerisation below 200 the tensile properties are very bad, from 300 up to 800 there is a steady improvement in these properties, but beyond 1,000 there is only a negligible further improvement. As the viscosity of cellulose solutions increases progressively more rapidly the higher the polymerisation, the highest usable viscosity sets a limit to the highest degree of polymerisation of the cellulose that can be used. This lies somewhere about 800 at present.

From Staudinger and Reinecke's data native cellulose fibres have a degree of polymerisation of 3,000 and modern wood pulps of 800 to 1,000. The regenerated cellulose rayons generally have lower values. Amongst rayons those made from cellulose nitrate had the lowest values for the polymerisation, which was between 115 and 200, normal viscose rayons have somewhat higher values of about 300, cuprammonium rayons have higher values again of about 550, whilst specially strong modern viscose staple fibres have the highest values of up to 800.

The idea of reducing the solubility in water and aqueous solutions of artificial protein fibres and simultaneously of improving their mechanical properties by introducing cross-linkages with formaldehyde is contained in Millar's, 'Todenhaupt's and Ferretti's processes' (*cf.* Protein Fibres, p. 115). A similar application of formaldehyde treatments to cellulose rayons was made by Strehlenert (B.P. 22540, 1896) and Eschalier (B.P. 25647, 1906), the latter's process being known as " sthenosing." More recently cross-links formed by formaldehyde–urea condensations and by the condensation of other substances in cellulose rayons, have been used to obtain " anti-crease " effects (Elöd and Etzkorn, Angew. Chem. 1938, **51**, 45). Cellulose fibres treated with resins in this way have reduced moisture adsorptions and resist solution in cellulose solvents such as strong sulphuric acid and cuprammonium hydroxide.

When fibres or fibre-forming materials are stretched, whilst the materials are plastic due to swelling or heating, the chain polymers are oriented parallel to the direction of stretching. When the plasticising influence is removed the chains set in their new configuration. The structure has increased strength and decreased extensibility in the direction in which the stretch was applied. Stretching during or after spinning is applied to all rayons with the object of improving their strengths.

A number of theoretical and experimental investigations have been made of the problems of stretching fibrous materials in general and cellulose fibres in particular (Hermans and collaborators, *l.c.*; Kratky and collaborators, Kolloid-Z. 1937, **80**, 139; 1938, **84**, 149, 268). Although the theoretical and experimental curves relating stretching to the anisotropy of swelling follow somewhat divergent courses, the maximum possible stretch is found to be about 1 : 2 in each case. This applies to swollen gels measured in the swollen state. If, however, the unstretched and maximum stretched fibres are dried, the ratio of length is then 1 : 4, since the unstretched fibres contract on drying much more than the stretched fibres. The former authors give curves showing the marked increase of strength of cellulose fibres as a randomly oriented fibre is stretched into one which is completely or nearly completely oriented parallel to the direction of stretch. Data on the effect of stretching the new polyvinyl-chloride rayon, vinyon, show that a 200% stretch gives an increase of wet strength from 0·8 to 3·2 g./den., whilst the wet extensibility decreases from 110% to 10% (Text. World, 1939, **89**, No. 7, p. 55).

It has been possible to measure the anisotropy of the tensile properties of stretched cellulose films (Mark, " Physik und Chemie der Cellulose," Berlin, 1932, p. 53), but no data are available for fibres because of the difficulty of making such measurements in any other direction than that of the fibre axis. In the case of cellulose fibres the anisotropy has been investigated and many other properties related to the orientation of the cellulose chains produced by stretching, and a number of relationships have been found. The most important anisotropic properties are: the anisotropy of swelling (Hermans and collaborators, *l.c.*); the refractive indices (Preston, Trans. Faraday Soc. 1933, **29**, 65); the dichroism of dyed fibres (Preston, J. Soc. Dyers and Col. 1931, **47**, 312); the polarised fluorescence of dyed fibres (Morey, " Report to the Textile Foundation," U.S.A. 1933; Text. Research, 1933, **3**, 325; 1934, **4**, 491; 1935, **5**, 105, 483).

The standard method of measuring the orientation of the chains is by photometric measurements on X-ray photographs obtained with copper radiation (Sisson, Ind. Eng. Chem. 1935, **27**, 51; Go and Kubo, J. Soc. Chem. Ind. Japan, 1936, **39**, 458B; Berkley and Woodyard, Ind. Eng. Chem. 1938, **10**, 451).

Visible Structure.—The influence of the fine structure is modified by the microscopically visible structure, of which the important factors are:

(1) The size and shape of the fibre cross-sections, which affect the flexibility, the covering power and the apparent depth of colour for a given concentration of dye.

(2) The presence of planes in the fibre surface not parallel to the fibre axis and optical heterogeneity in the fibres which reduce the lustre.

(3) The angle of twist of the fibres about the yarn axis, which also affects the strength and the lustre.

The size of rayon filaments and yarns is generally given in terms of denier, where the denier is the weight in g. of 9,000 metres of the filament or yarn.

Yarns with fine denier filaments are softer and more flexible than those with coarse filaments. There is practically no limit to the fineness or coarseness of the filaments that can be spun but the very coarse ones are only useful as artificial horse-hair and the very fine ones are difficult to spin and fragile in use, consequently for ordinary textile purposes a limited range of filament deniers from about 1 to about 6 are the only ones generally produced. Yarn deniers in common use range from 75 to 300.

Other conditions being constant fine filament yarns have a greater covering power and dye an apparently lighter shade with a given concentration of dye than do coarse filament yarns.

Normal rayons have solid homogeneous filaments, the surfaces of which are bounded by planes parallel to the filament axis. Such rayons possess the best lustre since there is the maximum possible gradient of brilliance with variation of the directions of illumination or viewing. Any planes in the surfaces of the filaments which are not parallel to the filament axis reduce the gradient of brilliance and thereby reduce the lustre. Optical heterogeneity in the interiors of the filaments operates in the same way (Preston, J. Soc. Dyers and Col. 1931, **47**, 136).

Normally the twist of rayons is so small (2–3 turns/in. in viscose, ½ turn/in. in acetate and no twist at all in cuprammonium) that the filaments lie nearly parallel to the yarn axis. In this condition rayon yarn shows the greatest lustre since the filament surfaces lie as nearly as possible parallel to the yarn axis. In crêpe twisted rayon yarns, containing twists up to 60 turns/in., the filament surfaces lie at all possible angles to the yarn axis with the consequence that light reflected from the yarn is scattered equally in all directions, the gradient of brilliance approaches zero and the yarn appears mat. For a similar reason rayon staple-fibre yarns, which contain a fairly high twist, though not such a high twist as crêpe yarns, have a lower lustre than " flat " continuous filament yarns.

When a yarn is twisted, the central filaments are merely twisted about their own axes, but the outer filaments have to follow a spiral path round the central core. The tangent of the angle of the spiral is proportional to the diameter of the yarn multiplied by the number of turns/in. Now since the length of the spirals of the outer filaments in a given length of yarn is greater the greater the spiral angle, twisting the yarn sets up stresses in the outer filaments which are relieved by these extending and the yarn as a whole contracting. Crêpe twisted yarns as a consequence have deniers 20–30% greater than the " flat " yarns from which they were twisted.

A further consequence of the spiral formation of the filaments in highly twisted yarns is that a stress applied to the yarn is unequally distributed amongst the filaments of which it is composed. With 150 denier yarns twists up to about 20 turns/in. have only a small effect on the strength, but with higher twists there is a progressive and rapid decrease of strength (Hamm and Cleveland, Bur. Stand. J. Res. 1931, **7**, 617). With staple fibre yarns some twist is necessary to bind the fibres together and to produce any strength at all. In this case the first effect of increasing the twist from zero is to increase the strength up to a maximum which depends on several factors and with normal yarns lies in the region of 20 turns/in.; beyond this increasing twist produces a similar decrease in strength to that found with continuous filament yarns (Ashton, J. Text. Inst. 1935, **26**, P16, P177).

Strength and Extensibility.—Strong and weak are terms freely applied to textile materials, but as ordinarily used they are rather vague descriptions. The textile quality they describe is one that is difficult to define quantitatively, partly because no absolute standards exist and partly because the significance of strength varies with the form and function of the textile material. Thus in a rayon yarn strength usually means the breaking load per denier under certain arbitrary conditions, whilst in a fabric the term strength is often used to denote ability to withstand the stresses encountered in normal use. Ultimately, of course, all stresses applied to a fabric must be borne by the yarns of which it is constructed, but the manner in which the stresses are distributed amongst the individual yarns will depend in part at least on their extensibility. Stresses will be better distributed and, consequently, there will be less chance of a breakdown occurring, with extensible yarns than with inextensible yarns. Effective strength is thus a function of both breaking strength and extensibility. For the foregoing reason the last-named properties taken together are a much better measure of the quality of a rayon than breaking strength alone. It is important to consider them together for another reason, because with any given rayon strength is directly and extensibility is inversely proportional to the degree of orientation. As a first approximation the product of strength and extensibility is constant with cellulose rayons of a given degree of polymerisation, independently of whether the values are for dry or wet material. Put in other words, the work of rupture is approximately constant as will be seen for example from the values given by Rose (*ibid.* 1939, **30**, 202). The effect of the degree of polymerisation on the work of rupture will also be seen from Rose's values for the specially strong "tenasco" rayons compared with normal rayon.

The breaking strength wet relative to the breaking strength dry is another function of the degree of polymerisation. The less the cellulose is polymerised the greater is the loss of strength on wetting. The degree of polymerisation of cellulose rayons made by different processes is indicated by their fluidities in cuprammonium hydroxide solution, where the greater the fluidity, the less is the polymerisation. Mean values from the fluidity data for various rayons given by Ridge, Parsons and Corner (*ibid.* 1931, **22**, T117) together with mean values for the relative wet strengths of similar rayons taken (i) from King and Johnson (J. Soc. Dyers and Col. 1928, **44**, 346), (ii) from Ridge and Bowden (J. Text. Inst. 1932, **23**, T319), and (iii) from Lilienfeld (B.P. 323731), together with values for the degree of polymerisation given by Staudinger and Reinecke (*l.c.*) are tabulated below.

	Fluidity of 2% soln. reciprocal poises.	Degree of polymerisation.	Relative wet-strength.
Lilienfeld viscose .	4·4	—	65% (ii), (iii).
Cuprammonium .	4·6	500	54% (i), 60% (ii).
Normal viscose .	10·5	300	50% (i), 45–50% (ii).
Nitrate	16·7	200	41% (i).

Ridge and Bowden (*l.c.*) have shown that increasing degradation of the cellulose of cuprammonium and of Lilienfeld and normal viscose rayons, as measured by fluidity, is directly proportional to the loss of strength both dry and wet. The dry and wet strength–fluidity relations run parallel, with the latter displaced towards the zero strength axis. Since for a given increase in fluidity both the dry and wet strengths fall by an equal amount, it follows that with higher fluidities the relative wet strength becomes smaller. Staudinger and Reinecke (*l.c.*) have published curves showing a similar relation between strength and fluidity, but in addition give values for the degree of polymerisation.

Since the early days of the industry there has been a steady improvement in the tensile properties of regenerated cellulose rayons. This has been mainly due to the production of yarns composed of progressively less and less degraded cellulose. From this cause modern rayons lose less strength on wetting than the older ones, as will be seen from the table shown at the top of the next column, also the breaking strengths are higher for a given extensibility with the modern than with the older rayons. In 1896 cellulose rayon regenerated from cellulose nitrate lost as much as 90% of its strength on wetting (Strehlenert, B.P. 22540, 1896).

Date.	Rayon.	Breaking strength g./den.	Relative wet strength.	
			%	
1901	Nitrate	1·17	19	Suvern, "Kunstliche Seide," 2nd ed., Berlin, p. 223.
1901	Viscose	0·8	23	Dreaper, J.S.C.I. 1909, **28**, 1297.
1922	,,	1·50	33	Rep. on the Dev. and Use of Rayon and other Syn. Fibres, U.S.A. 1938.
1927	,,	1·90	42	do.
1932	,,	2·0	50	do.
1937	,,	2·0	50	do.

The increasing use of stretch spinning has contributed to some extent to the increased strengths of modern rayon yarns, but when increased strength has been obtained in this way alone it has resulted in the production of yarns with small extensibilities. Stretch spinning was introduced into the cuprammonium process at an early stage, and as cellulose regenerated by this process was comparatively less degraded than that produced by the nitrate or viscose processes, this rayon used to have the best tensile properties (Staudinger and Reinecke, *l.c.*). The position has now been equalised between the cuprammonium and the better viscose processes. Exceptionally highly stretched yarns of comparatively little degraded cellulose were made by the Lilienfeld modification of the viscose process in England and abroad during the period 1926–30. These had dry strengths of 4·4–6·1 g./denier and very good relative wet strengths, but unfortunately their extensibilities were very small, only 4·3–6·5%, but most of this was elastic strain recoverable on removing the stress. The extensibilities of Lilienfeld but not of normal viscose rayons can be doubled without appreciably affecting the strength by treatment at 25°C. with 7% $NaOH$ (B.P. 323731). Highly stretched rayons made by various processes have reappeared on the market both in England and the United States, where they are finding a use in motor tyre fabrics. English yarns having dry strengths from 2·4 to 3·6 g./denier are reported by Rose (*l.c.*) and these yarns, as well as having very good relative wet strengths, have much higher extensibilities than the Lilienfeld yarns. These modern strong viscose yarns are claimed to have the added advantage of much higher elasticities than have normal viscose yarns. Yarns with remarkably high dry and wet strengths have been made by the British Celanese Company during 1939, but these yarns have low extensibilities.

Since the war (1914–18) rayon staple-fibres have shown similar improvements in tensile properties to those shown by continuous filament yarns. Jehle (Angew. Chem. 1938, **51**, 15) has given data for a number of German rayon staple-fibres of different dates and types. A selection from his values are shown in the table at the top of the next page.

Date.	Breaking strength.		Extensibility at break, dry.
	Dry.	Relative wet.	
1922–26 .	2·1 g./den.	46·5%	8·4%
1936–37 .	2·85 „	53·7 „	19·6 „

From what has been said earlier it is apparent that moisture affects breaking strength. It also affects extensibility. Generally the higher the moisture content the greater the extensibility, not only at a given load, but also at the breaking point. With the "wet" values the condition of the yarn is sufficiently defined in regard to humidity, but the condition of the yarn to which the "dry" values refer needs further qualification. Because of the experimental difficulties which would be encountered in testing perfectly dry rayon and because normal air-dry material contains an appreciable quantity of moisture, "dry" values refer to material which has been conditioned at 65% relative humidity (B.I.S.F.A. Rules for Viscose Cuprammonium and Acetate Rayon, 1938 Edition).

Tables of factors have been published for converting breaking strengths obtained at other than the standard humidity to the standard condition (King and Johnson, *l.c.*; Herzog-Wagner, "Physikalisch-technisches Faserstoff-Praktikum," Berlin, 1931, p. 114). These factors are of dubious value since they vary with different rayons, for example, they vary with the degree of polymerisation of the cellulose.

When making tensile tests the rate of loading is an important factor in the results obtained. The breaking strength found increases when the rate of loading or extension is increased (Hunter, Rayon Text. Monthly, 1936, **17**, 739, 805). The value obtained varies directly as the logarithm of the rate of extension (Bayes, J. Text. Inst. 1939, **30**, P210). Because of this all tests must be made at a standard, if arbitrary, rate of loading to obtain comparable results.

Temperature has a marked influence on the tensile properties of acetate rayon. Mark, "Physik und Chemie der Cellulose," Berlin, 1932, p. 50, gives values showing an approximately linear fall in breaking strength from 1·4 g./den. at 20°C. to 0·10 g./den. at 120°C. Breuer (Kuntseide, 1939, **21**, 324) publishes data showing that the temperature of the water used for wetting rayons when making wet tests has a marked influence on the results obtained. Increasing the temperature results in an increase in extensibility and a fall in breaking strength.

Tensile data for a large number of rayons of all types were published twelve years ago by King and Johnson (*l.c.*) from which it was clear that at that time cellulose acetate rayons were weaker than viscose rayons both when dry and when wet. More recent data given by Herzog and Koch, "Fehler in Textilien," Heidelberg, 1938, p. 6, show that normal acetate occupies the same relative position, although recently exceptionally strong acetate yarns have been reported (Textile World, 1939, **89**, No. 10, 80). Casein fibres' claim to commercial utilisation depends on their chemical properties, since their tensile properties are much inferior to cellulose rayon staple fibres in respect of wet and dry strength and are inferior to wool in respect of these properties and in respect of elasticity also (Spitalny, Waleschkewitsch and Ljaschtsch, J. Text. Inst. 1938, **29**, A263; Heim, *ibid.* 1939, **30**, P213; Diamond and Wormell, *ibid.* 1939, **30**, P224).

Elasticity.—For the first time since 1926 when Lilienfeld rayon was launched with the claim that it was a great improvement on its predecessors because of its remarkable tensile properties, a new rayon, "*Nylon,*" has been launched with similar claims. It is important to notice that the emphasis is different now from what it was fourteen years ago. In the case of Lilienfeld rayon the claim was justly made that here was a fibre with great strength, whilst in the case of nylon the claim is not merely that it has great strength but that in addition it has considerable extensibility and elasticity. The last item of the claim is most important since it is in respect of elasticity that all the other rayons are most defective compared to silk and wool. Thus although the extensibility of viscose rayons may range from 16 to 24% the elastic part of this is very small and similarly for acetate rayons the elastic part of the extensibility is only a little greater than that of viscose (Ohl, Textilber. 1933, **14**, 485). It is because of the small elasticity of cellulose rayons that they crease badly compared to the natural animal fibres. However, they can be greatly improved by the Tootal Broadhurst Lee Co.'s process (B.P. 291473) of impregnation with dimethylolurea which is subsequently condensed to a resin in the interiors of the filaments by heating. This treatment improves the strength and the crease-resistance and reduces the swelling of the filaments in water and the absorption of moisture at all humidities. The reduction of moisture content of the resin-impregnated fibres is an important factor in improving their elastic properties (Elöd and Etzkorn, Angew. Chem. 1938, **51**, 45), since it reduces the possibility of relaxation taking place with the formation of a stable deformation. From ordinary mechanical considerations the strains imposed on rayon filaments when they are bent will be smaller the finer these are, so that it might have been expected that these would show more resistance to creasing. However, although the reverse has been found by Quehl (Textilber. 1939, **20**, 76) his results are vitiated by the fact that he varied two factors simultaneously, the filament denier and the yarn denier.

Impregnation with synthetic resin is not a satisfactory method of rendering acetate rayons more resistant to creasing (Chwala, "Textilhilfsmittel," Vienna, 1939, p. 418).

As has been said earlier, the great claim made in respect of nylon fibres is that they have exceptionally high elasticity. This has been borne out by the published data. Up to an extension of 8% there is complete recovery on removing the stress and at 16% extension there is 91% recovery (Amer. Dyestuff Rep. 1939, **28**, 198). These data refer to stresses imposed for 100 seconds; stresses imposed for longer periods at extensions which are initially 15% or over will result in flow and there will be less perfect recovery when the stress is subsequently removed.

Vinyon fibres are also claimed to have good elasticity, but no data are available (Textile World, 1939, **89**, No. 8, 55).

Casein fibres have very high extensibility but poor elasticity in the dry state. For example, after stretching to 10% the recovery after 24 hours still leaves a 6% extension. The recovery is better in the wet state (Heim, J. Text. Inst. 1939, **30**, P217). A similar behaviour is found with regenerated cellulose rayons which show a much better recovery in the wet state; also if wetted after stretching, dry cellulose rayons will recover most of the original stretch (making allowance for the normal lengthways swelling when wet) (Weltzien and Götze, "Chemische und physikalische Technologie der Kunstseiden," Leipzig, 1930, p. 137). The latter behaviour is a very useful means of detecting the presence of latent strains in cellulose rayon yarns.

Typical data, collected from a number of sources, for tensile properties, moisture contents at 65% relative humidity, densities and melting points of various rayons are given in the table below.

Rayon.	Density.	M.P. °C.	Moisture absorption at 65% R.H.	Dry str. g./den.	Wet str./Dry str. %	Dry extn. %	Wet extn. %
Viscose normal . .	1·53	Chars	13	2·0	50	20	22
Viscose strong. . .	,,	,,	,,	3·5	65	9	18
Cuprammonium . .	,,	,,	,,	2·0	60	13	25
Acetate normal . .	1·33	250	6	1·3	60	20	30
Acetate strong . .	,,	—	,,	6·8	80	7	—
Casein	1·26	—	—	0·9	50	50	100
Nylon	1·14	240	4	5·0	88	20	30
Vinyon.	1·20	*65	(0)	3·4	—	11	—

* Softens at this temperature.

Identification.—The various classes of artificial fibres, cellulosic, protein and so forth, can be easily distinguished by the burning test combined with chemical confirmatory tests; but in order to distinguish between the different cellulosic rayons, viscose, cuprammonium and partially saponified acetate, and as a check on the burning and chemical tests, a microscopic examination is essential. A summary of preliminary identification tests is contained in the table on page 134.

When mixtures of rayons are present as in a staple fibre yarn the presence of a mixture is most easily detected and identified by a microscope. The strength, extensibility and elasticity dry and wet give valuable indications even if carried out quite roughly in indicating whether regenerated cellulose or cellulose acetate rayons are of the normal or highly oriented type or whether cellulose rayons have been given an anti-crease resin treatment. With delustred rayons the delustring agent may be an inorganic substance which can be identified by igniting or dissolving the rayon and examining the residue, or it may be minute air bubbles in the case of cellulose acetate or vinyon, or it may be some organic substance. Whatever tests are used, it should be emphasised that it is important that known samples should be available for comparison.

Bibliography.—Hard, "Romance of Rayon," Manchester, 1933 (historical); Königsberger, "Die deutsche Kunstseiden und Kunstseidenfaserindustrie in den Kriegs- und Nachkriegsjahren," Berlin, 1925 (historical and statistical); Flügge, "Kunstseide," Leipzig, 1936 (economic and statistical); Mortgat, "La Fabrication de la Soie Artificielle par le Procédé Viscose," Paris, 1930; Pellatt, "Viscose Rayon Production," Manchester, 1931; Lipscomb, "Cellulose acetate," London, 1933 (manufacturing processes); Kausch, "Handbuch der Azetylzellulosen," Munich, 1933 (general reference); Bodenbender, "Zellwolle Kunstspinnfasern," Berlin, 1939 (manufacturing processes); Courtaulds, "Fibro in the Cotton Industry," Coventry, 1938 (properties and uses); Weltzien and Götze "Chemische und physikalische Technologie der Kunstseiden," Leipzig, 1930 (general account); Süvern, "Die Künstliche Seide," 5th Ed., Berlin, 1926 (patent abstracts to about 1926); suppl., vol. I, Berlin, 1931 (patent abstracts, 1926–28); Faust, "Cellulose Verbindungen," Berlin, 1935 (patent literature to about 1935); Jentgen, "Laboratoriumsbuch für die Kunstseide-u. Ersatzfaserstoffindustrie," Halle, 1923; Dorée, "The Methods of Cellulose Chemistry," London, 1933 (Chemical Analysis); Herzog, "Die Mikroskopische Untersuchung der Seide und der Kunstseide," Berlin, 1924; Preston, "Modern Textile Microscopy," London, 1933 (microscopy); Mark, "Physik und Chemie der Cellulose," Berlin, 1932; Marsh and Wood, "An Introduction to the Chemistry of Cellulose," London, 1938; Staudinger, "Die Hochmolekularen Organischen Verbindungen Kautschuk und Cellulose," Berlin, 1932; Mayer and Mark, "The Chemistry of High-Polymers," London, 1939 (theoretical and fundamental).

J. M. P.

Rayon.	Burning test.	Solubility and swelling in:					Cross-section shape.
		Acetone.	Methylene chloride.	90% Phenol.	Cuprammonium hydroxide.	Cold conc. HCl.	
Cuprammonium	Burns readily. No bead. Smell of charred paper.	Insoluble.	Insoluble.	Insoluble.	Soluble.	Swells 200–300%	Circular.
Viscose	Ditto.	Insoluble.	Insoluble.	Insoluble.	Soluble.	Ditto.	Irregular numerous serrations.
Ditto. Anti-crease treated	Ditto.	Insoluble.	Insoluble.	Insoluble.	Insoluble.	Only swells after several minutes.	
Celanese strong yarn MV	Ditto.	Insoluble.	Insoluble.	Insoluble.	Soluble.	Does not swell.	Polygonal.
Cellulose triacetate	Burns. Black bead. Acrid acetic smell.	Soluble.	Soluble.	Soluble.	Insoluble.	Swells.	2, 3 or 4 large lobes, or rarely knuckle bone.
Cellulose acetate 51–56% acetyl.	Ditto.	Soluble.	Insoluble.	Soluble.	Insoluble.	Soluble.	
Ditto. Partially saponified	Burns like cuprammonium.	Partially soluble.	Acetone extract leaves film on evaporation.			Hollow filaments remain.	
Nylon	Shrinks from flame. Hard round bead. Burns if heated on spatula with amide smell.	Insoluble.	Insoluble.	Soluble.	Insoluble.	Soluble.	Circular.
Vinyon	Shrinks from flame. Irregular bead. Burns if heated on spatula with burnt paraffin smell.	Soluble.	Soluble.	Insoluble.	Insoluble.	Does not swell.	Knuckle bone.
Casein	Burns.	Insoluble.	Insoluble.	Insoluble.	Insoluble. Stained blue.	Slight swelling.	Circular or horseshoe.

The above data concerning solubility and swelling apply to observations under the microscope when the fibres are treated with the reagent for a time not exceeding 5 minutes.

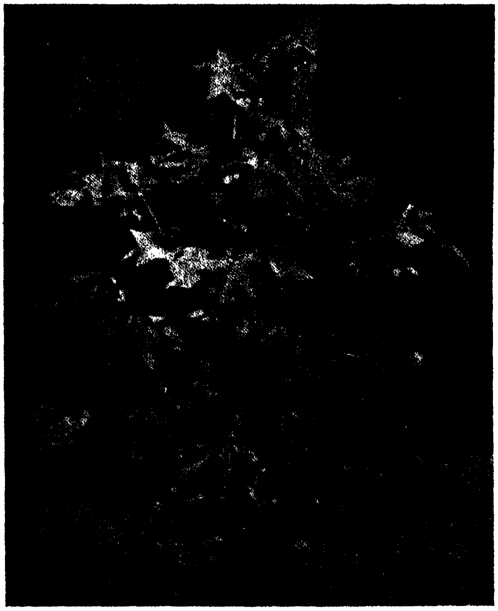
FIBRES, COTTON.—1. General.—Cotton consists of the long hairs covering the seeds of various species of *Gossypium*, a genus of the natural order *Malvaceæ*. The cotton plant grows as a small shrub or tree. It is of perennial habit, but is usually treated as an annual in cultivation to avoid damage by diseases and insect pests. In certain hilly districts of Brazil, however, tree forms are grown, which are allowed to remain in the ground for 7 or more years. When the flower-bud first opens, the flowers are generally white or creamy, but they gradually become dark red before falling to the ground on the third or fourth day. The young fruit remains attached to the flower stalk and enveloped in the calyx; it gradually increases in size and is known as the "boll." When the boll is ripe it dehisces in three to five sections (loculi), exposing the cotton which, with the release of the pressure, rapidly expands to form a large fluffy mass and is soon ready for "picking." The seeds, with the cotton fibre adhering to them, form the product known as seed-cotton; this is collected from the ripe bolls, and the cotton (or *lint*), after being separated from the seeds by a process of "ginning," constitutes the raw cotton of commerce. Seed-cotton usually consists of about one-third its weight of cotton fibre and two-thirds of seeds.

A cotton fibre consists of a single cell which, up to the opening of the boll, has the form of a long tube with a central canal, but much contorted in order to fit inside the cramped space available, for the seeds in a single large boll may bear as many as half a million fibres. When the fibres dry at the opening of the boll, they collapse into a ribbon form, and twist about their longitudinal axis. These natural twists or convolutions are peculiar to the cotton fibre, and occur sometimes in a right-handed and sometimes in a left-handed sense; the total number of convolutions in a fibre is composed almost equally of the two kinds and varies greatly from fibre to fibre even for a single variety, but ranges on the average from 4 to 6 per millimetre length; reversals of direction occur from once to twice per millimetre.[1, 2]

Owing to its economic importance, cotton has been the subject of a vast amount of study aiming at increasing production or improving quality of fibre, yarn and cloth. These aims, and the economic importance of the fibre, are illustrated by the further details classified under the following headings: (2) historical; (3) statistical; (4) distribution; (5) cotton varieties; (6) cotton growing; (7) yield of cotton; (8) diseases and pests; (9) development of lint hairs; (10) cotton quality; (11) chemical constituents of cotton; (12) cotton ginning and pressing; (13) cotton spinning—opening and cleaning, carding, combing, drawing, speed frames, spinning, doubling and twisting; (14) cotton yarn preparation; (15) sizing; (16) weaving.

2. Historical.—Cotton has been used for textile purposes since ancient times; references to it appear in early Hindu sacred books, and remnants of cotton string and fabric, identified by Gulati and Turner,[3] have been recovered from recent excavations of buried cities at Mohenjo-daro in the valley of the Indus, which archæological evidence shows to belong to a civilisation existing in 2750–3000 B.C.

3. Statistical.—During the past 100 years cotton has been the most widely used of all textile fibres; its annual crop exceeds that of all other textile fibres put together. Table I shows the average relative productions and the average prices of the different fibres for the 5 years 1932–37.



[*By courtesy of the McGraw-Hill Publishing Co.*

Fig. 1.

This high production of cotton has been developed during the last 150 years; before 1800 the world's crops amounted to less than 200 million lb., but had increased to 689 million lb. in 1835, to 5,030 million lb. in 1882, and to an average annual crop of 10,268 million lb. between 1902 and 1922. For the three quinquennia since 1922 the average annual cotton crops, including linters, have been—in million lb.—

1922–27.	1927–32.	1932–37.
12,203	13,434	13,616

Linters are the short remnants of cotton fibres, useless for spinning, left on the seeds in saw ginning and afterwards removed by a second saw ginning; in recent years linters have amounted to some 500 million lb. per annum.

The cotton production in recent years is compared with that of the other important textile fibres in Table II.

Table II shows how in recent years the synthetic rayon fibres have assumed much greater

Table I.—Relative World Production and Average Prices of Textile Fibres.[4]

	Percentage of total production.	Average price, pence per lb.	Quality.
Cotton	53·5	6·2 5·2 8·5	American Middling. Indian Superfine Oomras. Egyptian Sakellaridis. FGF.
Wool	15·3	27·6 12·0	Merino, greasy 66's. Crossbred, greasy 46's.
Jute	13·1	1·9	First marks.
Flax	6·8	6·8 10·2	Livonian ZK. Belgian.
Hemp	2·9	1·8 6·0	Indian (H.J.F.). Italian (Pi/SB).
*Leaf fibres	4·3	2·2	E. African Sisal No. 1.
Rayon	3·2	33·4	150 denier Viscose yarn (excise duty deducted).
Staple fibre	0·4	11·0	Viscose.
Silk	0·5	97·9	Japan 13/15's.
	100·0		

Average annual total production of textile fibres 1932–37 : 25,500,000,000 lb.

* Leaf fibres are Sisal, Manila hemp, New Zealand hemp.

Table II.—Production of Textile Fibres, in Million Lb.[4]

Year.	1929–30.	1930–31.	1931–32.	1932–33.	1933–34.	1934–35.	1935–36.	1936–37.	1937–38.
Fibre:									
*Cotton . . .	13,189	12,786	13,605	11,748	13,166	11,804	13,174	15,484	18,995
Wool (greasy) .	—	3,842	3,842	3,857	3,742	3,566	3,713	3,867	3,864
Jute	4,180	4,540	2,275	2,880	3,245	3,460	2,964	3,895	3,524
Flax	1,364	1,413	1,522	1,332	1,511	1,520	1,689	1,690	1,805
Hemp . . .	1,151	1,073	853	729	717	705	737	825	844
Leaf fibres . .	1,120	1,009	930	988	1,014	1,069	1,198	1,275	1,360
Silk	134	130	126	116	122	125	121	119	121
Rayon filament .	437	453	501	525	666	773	928	1,015	1,200
Staple fibre . .	8	6	8	21	29	53	140	299	622

* Excluding linters.

importance and a rapid increase in production; staple fibre, made in short lengths (23–16 in. long) on the same machinery as rayon filaments, for spinning on cotton spinning machinery, has also shown a most rapid expansion, though cotton continues to hold its own.

4. Distribution.—Cotton is grown in every continent, though in Europe and Australasia the crops are small; the relative importance of the various sources of supply is illustrated by the summary of recent crops given in Table III (average over 5-year periods for 1916–36 based on figures given by Todd [5]) which shows particularly how cultivation has extended in South America (Brazil, Peru and Argentina), in Asia and Europe (India, China and Russia), and in Africa (Egypt, Sudan, East Africa—Uganda, Tanganyika, Nyasaland and Kenya, and West Africa—Nigeria, Belgian Congo, etc.).

5. Cotton Varieties.—The botanical classification of different varieties cannot yet be said to rest on a satisfactory basis. Certain morphological features have usually been taken as the basis, the most instructive, according to Watt,[6] being "derived from the position and condition of the bracteoles; the presence or absence of nectar-yielding glands, and the nature of the floss and fuzz that surrounds the seed."

In accordance with this scheme, he divided the species of cotton into five sections, thus:

I. Fuzzy seeded cottons with no lint; *e.g. Gossypium Stocksii*, *G. Sturtii* (wild).
II. Fuzzy seeded cottons with united bracteoles: *G. Neglectum, arboreum, herbaceum* (Asiatic).
III. Fuzzy seeded cottons with free bracteoles: *G. hirsutum*, *G. peruvianum*, *G. mexicanum* (American).
IV. Naked seeded cottons, with the bracteoles free or nearly so, and glands conspicuous: *G. barbadense*, *G. brasiliense*.
V. Naked seeded cotton with bracteoles quite free and floral glands absent: *G. Kirkii* (wild; tropical E. Africa).

It should be noted that although *G. hirsutum* is now widely distributed, the original parents in every case appear to have been Upland American in origin. The transplantation has not been effected without a radical change in the cha-

TABLE III.—PRODUCTION OF RAW COTTON IN MILLION LB.

	1916–21.	1921–26.	1926–31.	1931–36.	1936–37.	1937–38.
America:						
*U.S.A.	5,965·3	5,758·8	7,416·8	6,342·0	6,199·5	9,473·0
Mexico	83·6	93·5	121·6	103·1	186·5	155·0
Brazil	195·1	282·8	251·5	515·1	856·0	1,141·0
Peru	69·6	95·1	119·5	148·1	184·5	148·0
Argentina	7·3	32·0	55·7	116·4	72·0	140·5
Others	5·5	29·2	33·7	31·4	65·5	65·0
Asia (Europe):						
India	1,748·6	2,161·8	2,178·9	1,964·9	2,526·8	2,265·2
China	1,078·2	964·6	1,010·5	1,202·3	1,870·5	1,541·5
Japan, Korea	36·3	54·3	71·0	90·6	92·5	150·0
East Indies	12·9	11·3	7·9	7·2	8·0	8·0
Russia	273·1	152·2	582·1	958·5	1,775·0	1,891·0
Persia	51·4	37·7	45·2	64·3	80·5	80·5
Iraq, Ceylon, etc.	—	0·6	1·6	0·7	4·0	8·0
Asia Minor and Europe	53·6	43·4	61·4	105·2	172·0	218·0
Africa:						
Egypt	556·8	656·9	783·4	719·5	910·5	1,101·0
Sudan	8·3	21·3	57·1	86·0	133·0	122·5
E. Africa (British)	20·6	59·6	76·3	132·9	174·5	173·0
S. Africa (British)	0·8	5·6	4·8	1·3	1·5	1·5
W. Africa (British)	7·7	11·7	11·5	14·3	19·0	12·5
Non-British	4·7	22·0	49·2	76·5	133·5	135·0
W. Indies (British)	2·0	1·7	2·3	1·5	2·0	2·5
W. Indies (Non-British)	5·2	10·0	11·4	13·8	12·5	12·5
Australia, etc.	0·3	3·8	3·8	6·1	4·5	10·0
	10,186·9	10,499·9	12,957·2	12,701·7	15,484·3	18,855·2

* Excluding linters.

racter of the lint arising from the environmental upheaval. Temperature, mean length of day, angle of incidence and duration of solar radiation, combined possibly with radical changes in the frequency and extent of watering—have generally resulted in the African- and Asiatic-grown ***hirsutum*** cottons failing to obtain the degree of maturity characteristic of the original Upland Americans.

The advances in cytology in the present century have led to a new orientation of view regarding the species of *Gossypium*. Two main divisions of the genus are clearly defined according to the number of chromosomes † in their nuclei ; these divisions correspond generally with the geographical division into Asiatic and American types ; the Asiatic types have 13 chromosomes and the American types 26 chromosomes in the cell nucleus.[7] All the cultivated types fall into one of these two great divisions, though by cross-breeding it has proved possible to produce cottons having other numbers (39 and 52)[8] ; and a more detailed classification of cottons has been put forward in accordance with modern genetic and taxonomic knowledge.[9, 10] However, even the new detailed classification of *Gossypium* species cannot yet be regarded as complete.

Recently, the sole member of Watt's Section V, *G. Kirkii* had been excluded from the genus *Gossypium*, and renamed *Gossypioides* on the grounds that it differs from all the other species in neither grafting nor crossing with them, and in having a square stem[9] ; this exclusion is strengthened by the discovery that it has only 12 chromosomes.[8]

According to Skovsted,[11] the Asiatic cottons have 13 large chromosomes of much the same size, the American cottons 13 large and 13 small chromosomes, the small ones being little more than half the length of the large ones. Some American wild cottons have only 13 chromosomes of the same size as the *small* ones in the American cultivated types. For this reason Skovsted concludes that the American cultivated cottons of 26 chromosomes have been derived from a cross between two species of *Gossypium* both having 13 chromosomes, but one set being of the large type like the Asiatics and the other of the small type like the American wild types.

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† Chromosomes—the genetic elements that together make up the nucleus of a cell; separating when the cell of growing tissue is about to divide, themselves dividing, and one of each pair re-assembling to form two nuclei, one for each of the daughter cells. When the first sexual cells are formed in a plant, the chromosomes of the nucleus separate into two groups without preliminary division, and each group forms the nucleus of a daughter cell; thus the nucleus in this haploid phase has only half the number of chromosomes present in the nuclei of cells of vegetable tissue. These daughter cells divide and re-divide many times, but nuclei of the new cells have a chromosome composition similar to their own ; but when fertilisation occurs and the sexual cells unite to form a new cell the nucleus of this cell has the full number of chromosomes (diploid phase) which is repeated in the nuclei of cells formed from it in the subsequent vegetative division and development. The number of chromosomes referred to in the discussion is, throughout, the haploid, or reduced number.

6. Cotton Growing.—The chief physical requirements for cotton growing are suitable soil, temperature and water-supply; where the first of these is not naturally suitable, more particularly where long-continued growing has impoverished the soil, otherwise suitable in texture and depth, the deficiency in composition may be made good by manuring (U.S.A.). The temperature requirement restricts the growing to tropical and sub-tropical regions of the earth's surface. Where the rains are not a natural source of water-supply, the deficiency may be made good—at high cost—by irrigation (Egypt, Sudan, India, U.S.A.). Where irrigation water is available, the seasonal temperatures may be utilised to best advantage; in regions dependent on a "rainy season," this determines the sowing time; under irrigation, the temperature. Often the harvest time ("picking") is determined by the incidence of frosts which kill the cotton plants. Thus the growing period may be definitely limited at the two extremes by climatic conditions; in such circumstances the varieties chosen for growing must have a growing period suitable for the conditions, so that the seed-cotton in the bolls, the last natural phase of the plant's activity, may have an opportunity to mature. These simple criteria are all illustrated by conditions in India: under irrigation in Sind and the Punjab, the soil temperature is suitable for seed germination in early April, frosts may occur in December, and picking proceeds from October onwards; in the central Indian belt, under rain-fed conditions, sowing takes place during the first break after the early monsoon rains in June, picking in September onwards, though further west, in Broach and Surat, the growing period is much longer as more equable conditions prevail near the coast and picking takes place in April onwards. In South India sowing occurs after the breaking of the north-east monsoon in August, with picking in April to July.

7. Yield of Cotton.—The monetary return to the farmer for his outlay and labour on any given area is determined by two primary factors—the yield or the quantity of lint produced and the quality of that lint. As already indicated, yield is a complex quantity: it depends both on the variety and its environment. Good soil and good cultivation, coupled with favourable climatic conditions, may provide a suitable environment; the next step is to choose a variety of cotton nicely matched to that environment. Good cultivation includes not only good agricultural practice generally in draining and tilling the soil and caring for the crop, but also a proper choice of sowing date, distance between the plants and time and extent of watering if the crop is an irrigated one. In the choice of variety, the growing season, which limits the time available for the crop to mature, must be a first consideration; the stand, or the number of plants that come to maturity, is another important agricultural factor; with a given number of plants to the acre, the yield per acre evidently depends on the average yield per plant, and this in turn on the number of bolls (or seed-pods), the number of seeds per boll and the weight of lint per seed. Varieties that are bushy are naturally not planted so closely as more slender varieties; and the contributory factors may differ considerably from one variety to another. Thus the Cambodia and Nandyal cottons, both grown in the Madras Presidency of India, have average values as follows:[12]

Variety.	Spacing.	Bolls per plant.	Seeds per boll.	Weight of seed mg.	Weight of lint per seed, mg.	Weight of lint per plant, g.
Cambodia Co. 2 (*G. hirsutum*)	36 in. × 9 in.	8	35	136	76	21·3
Nandyal 14 (*G. Indicum*)	18 in. × 9 in.	27	21	46	14	7·9

Climatic conditions have not only a direct physical or physiological effect on yield through the temperature and water-supply, but also an indirect effect through the incidence of diseases and pests.

Generally speaking, the object of the grower is to bring as many bolls as possible to maturity before some limiting factor operates to cause cessation of growth. To this end the early flowering varieties are favoured, as leading to early fruiting. Now certain branches of the plant (monopodia) do not bear flowers directly, but only vegetative organs (or further branches), whereas other branches (sympodia) bear flowers as well as vegetative organs, so that one object of selection is the isolation of varieties bearing sympodia at an early stage of their life history. If the sympodia are borne early on the main monopodial stem—between the 5th and 15th nodes, the plant has a "sympodial habit"—if the sympodia only appear between the 20th and 50th nodes, it has a "monopodial habit": if the sympodia begin to appear between the 15th and 20th nodes, the habit is "intermediate."

8. Diseases and Pests of Cotton.[13, 14]—Diseases and pests take a tremendous toll of the cotton crop; their depredations are not only responsible for many plants failing to come to complete fruition, but also for much of the cotton produced being greatly diminished in value owing to damage or staining by these agencies. It has indeed been said that the different grades of Egyptian cotton, which being grown under irrigation escape many sources of damage arising from untimely rains, are an exact expression of the amount of pink boll-worm attack.

Diseases.

Cotton Wilt (*Fusarium vasinfectum*) is the most widespread disease to which cotton is subject; it is a fungal disease with greater incidence in regions of heavy rainfall: the development of wilt-resistant varieties is the method usually adopted to combat it. There is some reason to believe that the wilt disease is not due to the same fungus in India as in America. The symptoms are wilting of the plant's vegetative organs, woody parts of stem turning brown or dark coloured.

Black Rust is a physiological trouble common on the poorer soils of the U.S.A. belt, due to improper soil conditions.

Cotton Anthracnose which attacks all parts of plants except large roots, is a fungal disease affecting the plants at all stages of their growth; on the bolls it starts as small dull red spots, gradually enlarging and finally affecting the boll contents.

Root Knot is caused by a nematode, a small eel-like worm that enters the roots and leads to root swellings, especially in light sandy soils; it has been stated to be second only to wilt as a disease causing damage in U.S.A.

Angular Leaf Spot or *Blackarm* is a bacterial disease of cotton, known as the former when it attacks leaves (as in U.S.A.) and as the latter when it attacks stems or branches (as in the Sudan and other parts of Africa).

Insect Pests.

By far the most damaging insect pests of cotton are the Mexican boll weevil (*Anthonomus grandis*) of U.S.A., and the pink boll worm (*Platyedra* or *Pectinophora gossypiella*) common in most cotton-growing countries, especially Egypt, Brazil and India. The boll weevil entered Texas from Mexico in 1892, gradually spread east and north, and by 1921 had practically covered the whole cotton belt in the U.S.A.; the weevil is a dark brown insect, up to about a quarter of an inch long; its life cycle is about 3 weeks; it seldom lives more than 7 weeks in summer, though occasionally much longer—up to 6 months or more. The weevils attack the unopened flower buds for preference, but when these become scarce they attack young bolls. The direct annual loss in U.S.A. through the boll weevil is immense, and was estimated in boom years to reach £100,000,000. The weevils hibernate through the winter and a cold winter largely reduces their numbers; so does a hot summer: poisoning them by calcium arsenate, sometimes dispersed as dust from aeroplanes, is the favoured remedy.

The pink boll worm was first described by Saunders in 1842 from Indian specimens; it was reported in Egypt 1906–7, Brazil 1911–13, Mexico 1911, Texas 1916. Its damage to the Egyptian crop alone has been estimated at £6,000,000 annually. The larvæ enter seeds and eat their contents; the infested seeds fail to develop fully and the lint is often stained pink and may be short and weak. The worm is the larval stage of a small brown moth, having wings of about ¾ in. span; the life-cycle is about 5 weeks in summer. The worms, on hatching from the eggs, tunnel into the bolls. Carbon disulphide poisons them, but the only satisfactory remedy is heat treatment of the seed, now compulsory in Egypt.

Life cycle:	Stage:	Egg	Larva	Pupa	Adult
	No. of days:	4/12	20/30	10/20	14/20

Other pests are the cotton leaf worm (*Alabama argillacea*), for which arsenical preparations are a remedy; the cotton boll worm and cotton red spider (really a small leaf-sucking mite) affect U.S.A. crops, and are controlled by insecticides; cotton stainer (*Dysdercus* species) is a very widespread foe, known in U.S.A., India and Africa. Other leaf-sucking insects are *Jassids*, a most serious pest in South and East Africa, and the *Whitefly* (Punjab).

9. Development of Lint Hairs and Quality of Lint.—Lint hairs only begin to be formed comparatively late in a cotton plant's history. To take an Egyptian plant as an example[15]: a seed sown on March 28th, germinated in 7 days (April 4th) and the first flower buds appeared after another 47 days (54 days from sowing); the first opening of flowers occurred after a further 31 days (85 days from sowing). From the time of opening of the flowers until the bolls opened—the "boll maturation period," during which the lint hairs lengthen and thicken—some 52 days elapsed.

In the case of this plant, therefore, the period from planting to flowering was 85 days, and for boll development 52 days; bolls of different ages on the same plant came to maturity over a period of 60 days, so that from first to last bolls are developing over a period of 112 days. Whilst 137 days elapsed before the first boll completed its development, other bolls continued to develop over the succeeding 60 days—the life period of the whole plant thus being 197 days, or 6½ months.

The development of the lint hairs is naturally affected by the health of the plant; but although the number of flowers set and bolls produced—and so the yield—may be greatly affected by differences in environmental factors before flowering occurs, yet the *quality* of the lint depends almost entirely on the conditions subsequent to flowering. The development of the cotton fibres has been described by Bowman,[16] Balls,[17] Gulati,[18] Sheffield,[19] and others.

Lint hairs are part of the outer epidermis of the ovule; being in effect part of the vegetative tissue of the seed, they belong to the same generation as the plant which bears the seed. If the particular seed has been cross-fertilised, this will not affect the lint on that seed, but only the lint borne on the plant obtained when the seed is sown.

Some lint hairs are differentiated as such in the outer epidermis of an ovule even before it has been fertilised, others are differentiated later, up to the 10th day after fertilisation. The fibres lengthen for the 24 days ensuing upon fertilisation, growth being comparatively slow for the first 6 days, but much more rapid for the next 15 days, slowing down again for the final 3 days of the lengthening period. At this stage the fibre is fully grown in length, but the walls are exceedingly thin, consisting of the original cuticle with a layer of primary cellulose, and embedded wax. For the next 24 days deposition of secondary cellulose occurs on the inner side of the walls, in the form of daily growth-rings,[20, 21] as a result of diurnal variation in the conditions of growth; each growth-ring, according to Balls, consists of some 100 fibrillæ laid down spirally, and responsible for the convolutions, reversals, and wall-pits in the dry fibre; thus each cotton fibre comprises some 2,400 fibrillæ.

Evidently, interference with the plant's well-being during the period after flowering affects the *quality* of the lint; growth of lint, if arrested for a time, may be resumed after the set-back, but the loss during the period of arrest is not made good afterwards. In the case quoted above, bolls—and lint within—were developing over a period of 112 days: a set-back to the plant at any time within this period must affect some of the lint; in the middle of the period —56 days after the first flowering—the flowers that opened during the first 8 days of flowering would have come to boll maturity, and so be unaffected by the set-back; but those that opened between the 9th and the 56th days would be in various stages of thickening and lengthening on the 56th day, and their development would be interfered with accordingly, some would be rather thin-walled, others rather short. The actual effect depends on the severity and duration of the set-back. If very severe, lasting, say, 48 days, there would be all grades between normal and very thin-walled and very short. Such set-backs naturally occur from time to time in individual localities, with consequent effects on the fibres comprising the crop, especially the last pickings.

Conditions in some cotton-growing districts are such that the crop as a whole is harvested with a large proportion of the fibres incompletely thickened; American Upland cottons from which selections have been made through many generations in the Punjab in India, and in various parts of Africa (Uganda, Tanganyika, N. Nigeria, etc.), are especially prone to this character. Tests of quality have therefore been devised which include some measure of the maturity of the fibres.

10. COTTON QUALITY.—In the trade, the quality of a cotton is determined by a hand-and-eye examination. The amount of foreign matter is estimated directly by eye, and in case of doubt, by comparison with certain reference samples known as "standard grades." Staple length is judged by drawing out a hand sample between both hands and extracting tufts from the fibres exposed at the "fracture." Breaking a small tuft by a snap method after gripping the tuft by the thumb and index finger of each hand, gives an indication of fibre strength. The resistance offered by the hand-sample when being drawn out between the two hands indicates the "drag," "body," or "hardness" or "softness" of the cotton—properties which have a distinct bearing on its spinning capacity. Notice is also taken by eye of lustre or bloom, colour and the presence or absence of "neps," which commonly consist of small aggregations of immature hairs that spoil the appearance of yarn and cloth, especially in the dyed state.

In the laboratory, less subjective methods are available for assessing many of the qualities of a cotton sample. The quantity of foreign matter present may be found by means of the Shirley Analyser, the principle of which depends on the difference in buoyancy of the opened lint and the trash: the lint is first completely opened to the single hair stage by means of a saw-toothed roller (known as a "taker-in" type of beater), and then the whole is projected into a stream-lined airflow of narrow depth in which the cotton hairs are buoyant, whereas the trash falls through; the lint is collected on a perforated cage and the trash in a convenient settling chamber.

A general test (the "Combined Stapling Test"[22]) for judging the quality of staple, measures three fibre-characters: the length, the fineness and the maturity. Every sample of raw cotton consists of fibres of many different lengths; if these are laid down, the longest first and then the others in order, at right angles to a base line, the outline of the other ends of the fibres forms an ogive curve. For the measure of length, the upper quartile of this curve is preferred, taken when the short fibres or fibres less than half this length are neglected: this upper quartile is styled the "*effective length*" and corresponds very closely with the trade judgment of the *staple length*, as applied to the variable sample. As a measure of fineness, the *hairweight per unit length* (inch or cm.) is used. To measure the maturity, a number of fibres on a microscope slide are treated with 18% $NaOH$, and classified microscopically into three classes (normal, thin-walled and dead, otherwise mature, half-mature and immature): the treatment with $NaOH$ causes swelling, as a consequence of which the mature hairs lose their convoluted appearance, while the dead or immature hairs become strongly convoluted: the thin-walled or half-mature hairs develop just one or two convolutions here and there. What might be described as a normally mature sample of cotton comprises some 67% mature, 26% thin-walled and 7% dead hairs. As already indicated, values for the crops of different growing areas depend very much on actual conditions of growth, and a particular farmer's crop in any one such area may differ considerably from that of his neighbours, or what may be the usual crop. Subject to this qualification the values in Table IV for staple length, hair weight and immaturity, may be regarded as typical. This table also includes the approximately highest standard warp counts[12] for which the cottons are commonly used, and the lea strengths at these counts. (The *lea strength* is the strength of a skein of yarn, consisting of 80 threads having a perimeter of 54 in., placed on hooks 27 in. apart so as to form a test-specimen of 160 threads, which are then loaded until breakage occurs; after a few threads have broken the rest draw out without further increase in the load, which is registered on a dial.)

Reference to the physical properties does not always permit a decision as to the value of a sample for commercial purposes; cases sometimes occur when two cottons that respond alike to the physical or dimensional tests behave differently in spinning.

The ultimate test of the value of a sample of cotton is how it behaves in use. That certain cottons are specially suited to certain purposes is fully recognised; thus Sea Island cotton is

TABLE IV.

Cotton.	Staple length 32nds in.	Hair-weight per cm. 10^{-5} mg.	Per cent. mature hairs and per cent. dead hairs.	Suitable counts.	Lea strength, lb.
Sea Island (W. Indian) . .	54	123	55 17	240*	10
American:					
Memphis	40	186	45 16	50	42
Texas	31	208	49 12	24	79
Boweds	28	239	79 5	16	118
Brazilian.	36	191	50 12	40	39
Peruvian Tanguis	44	236	69 6	40	42
Egyptian:					
Sakellaridis	46	142	58 8	80*	31
Giza 7	44	146	61 8	80*	28
Uppers	38	185	69 6	50	39
Sudan Sakellaridis	46	132	65 12	80*	30
Sudan American	39	167	54 28	50	42
Uganda	37	154	35 25	50	42
N. Nigeria	34	176	51 21	40	50
S. Nigeria (Ishan)	39	275	71 5	40	36
Indian:					
Bengals	20	318	68 6	6	48
Oomras	22	278	62 8	12	80
Broach	24	263	76 12	16	60
Surat 1027	31	228	52 15	30	48
Punjab-American . . .	28	164	49 27	20	70
Cambodia	32	188	50 25	30	46
Tinnevellies	26	211	65 15	16	63
Coconadas.	24	239	79 7	14	80

* "Combed quality."

much used for the finest hosiery underwear, having an excellent soft feel and an appealing sheen; for coarser hosiery the white Peruvian cotton, known as Tanguis, is very suitable. But in large classes of other goods the dominant criterion for selection of cotton is price. Since long fine cottons are more expensive to produce than short coarse ones, so the price of goods made from the long cottons is necessarily higher than that of goods made from the coarse ones, though for some usages the coarse cottons may be intrinsically more suitable. Under present conditions, however, the commercial valuation of a sample of cotton is related directly to the fineness of yarn to which it can be spun, and for this reason it is customary to regard a "spinning test" as the best test at present available for judging the value of a cotton. Special techniques have been worked out for such "spinning tests" which are generally based on the results obtained by processing a 10-lb. sample on cotton spinning machinery of the standard type used in the industry, as described later (*v.* COTTON SPINNING).

11. **CHEMICAL CONSTITUENTS OF COTTON.**—Proximate analyses of dry cotton show that it consists of some 91% cellulose, 1 to 1·5% mineral matter, 0·3 to 0·5% wax, 1·2 to 2·4% protein, and up to 5% of matter of as yet undetermined composition (*v.* BLEACHING).

From the description already given of the development of the cotton fibre, and the effect of the conditions of growth on the physical properties, it is only to be expected that the chemical constituents—especially the minor ones—will also be affected in their relative quantities by the conditions of growth and the extent of development of the fibres (see below for variations in the percentages of constituents). Unfortunately workers on chemical constituents until recently disregarded the physical characters, and it remains uncertain whether or not their material and their results can be regarded as completely typical.

Chemical analyses of cotton have aimed at establishing differences between samples of cotton of different origin by means of their variable non-cellulose constituents. As will be seen from the details given below of determinations of cotton wax, nitrogen and phosphorus contents, ash, and copper number, the native Indian cottons are distinguished from other types by these values, and the Egyptian and American cottons differ in their phosphorus content.

For the properties of cellulose and compounds related to it—oxycellulose, hydrocellulose, cellulose esters, etc.—(*v.* CELLULOSE, Vol. II, pp. 456–474).

Cotton Wax.—The wax of the cotton fibre which lies mostly on the surface, but also apparently embedded in the cell wall, has been given the name "cotton wax" by Schunck[23]; the wax renders the cotton incapable of absorbing water readily. Lecomber and Probert[24] have determined the amounts and characteristics of the waxes of cottons of different origin, some of their results being:

	Amount per cent. on dry cotton.	Melting point or range °C.	Acid value.	Saponification value.	Unsaponifiable matter per cent.	Iodine value.
American:						
Upland	0·35	80·5	21	76	66	20
Delta	0·49	76·5	29	57	68	27
Mean of 12 samples .	0·44	75·5–80·5	25	66	64	22
Egyptian:						
Uppers	0·35	78·5	26	67	55	26
Sakellaridis . . .	0·43	77	31	81	50	—
Mean of 7 samples . .	0·39	76·5–80	27	78	54	23
Sea Island (W. Indian):						
Mean of 2 samples . .	0·51	78·5–79	21·5	61	61·5	23
Peruvian:						
Tanguis	0·29	79	23	55	64	25
Brazilian:						
Pernams	0·54	77	35	82	53	30
Mean of 5 South American samples .	0·41	76·5–79	30	71	60	25
Indian:						
Bengals	0·34	68	40	126	43	30
Oomras	0·30	68	38	148	41	32
Broach	0·33	70	37	120	45	28
Surat	0·42	69·5	39	96	51	34
Mean of 6 samples . .	0·34	68-72	38	121	45	32

The Indian waxes differ markedly in their properties from the other waxes, especially in their saponification value.

The specific gravity of all the waxes examined fell within the range 0·970 to 1·005, each extreme value being for an Upland American cotton.

The cotton waxes[25, 26, 27, 28] consist largely of free wax alcohols, chiefly gossypyl alcohol, $C_{30}H_{62}O$, and montanyl alcohol, $C_{28}H_{58}O$, with small quantities of alcohols, $C_{32}H_{66}O$ and $C_{34}H_{70}O$, and glycols, $C_{30}H_{62}O_2$ and $C_{28}H_{58}O_2$; in addition free acids are present—palmitic and stearic—with smaller amounts of carnaubic acid, and very small amounts of gossypic and montanic acids, oleic acid, and the acids $C_{34}H_{68}O_2$ and $C_{32}H_{64}O_2$. Palmitic acid, stearic acid, oleic acid, carnaubic acid and small amounts of higher acids occur as esters, the first three as glycerides and carnaubic acid as a phytosterol ester. Very small amounts of hydrocarbons and resinous substances are also present in the wax.

Proteins of Cotton.—The protoplasmic contents of the cotton fibre may be estimated from the nitrogen content, for which the following values for per cent. nitrogen have been obtained by Ridge[29]:

American: Texas 0·204; Long staple Upland 0·204; Georgian 0·221; Arizona (Egyptian seed) 0·399.

Egyptian: Uppers 0·291; Sakellaridis 0·315.

Sea Island (W. Indian): 7 samples, range 0·262–0·290. Mean 0·278.

Peruvian: Tanguis 0·184, 0·216. Mean 0·200.

Brazilian: Pernams 0·260; Ceara 0·221.

Knecht and Hall[30] found values of 0·204% for American and 0·248, 0·262% for Egyptian; Higgins[31] found 0·180% for American and 0·275% for Egyptian.

The phosphorus content of cotton has been studied by Geake[32] with ranges and mean results as follows for per cent. P_2O :

American: Texas 0·042; Georgian 0·044; long staple Upland 0·061. Mean 8 samples, 0·051.

Egyptian: Uppers 0·077, 0·089. Mean 7 samples, 0·094.

Sakellaridis 0·134, 0·117, 0·105. Mean 3 samples, 0·119.

Sea Island (W. Indian): 0·057, 0·068. Mean 11 samples, 0·067.

South American: Peruvian Tanguis 0·54, 0·63; Brazilian Pernams 0·077. Mean 6 samples, 0·068.

Indian: Bengals 0·071; Oomras 0·054; Broach 0·124; Surat 0·118.

Ash of Cotton.—The ash content of cotton has frequently been studied. Fargher and Probert's results,[33] with those of others quoted by them, are given at the top of the next page.

Type of cotton.	Ash (per cent.)							Ash alkalinity per gram of ash.	
	Davies and Dreyfus.[34]	Monie.[35]	Mitchell and Prideaux.[36]	Barnes.[37]	Fargher and Probert.[33]			Fargher and Probert.[33]	
					No. of samples.	Range.	Mean.	Range.	Mean.
Sea Island	1·25	1·1	2·2	1·2	6	0·7–1·2	1·0	14·4–15·8	15·2
American	1·5	1·6–2·1	2·0	1·3–1·9	12	1·1–1·3	1·2	13·1–15·7	14·1
South American	1·2–1·7	1·2–2·0	2·1	—	7	0·8–1·3	1·2	12·8–15·3	14·3
Egyptian	1·2–1·7	1·6–1·8	—	1·4–1·5	6	1·1–1·3	1·2	14·9–15·6	15·3
Indian	2·5–6·2	2·3–5·3	2·9–3·3	1·3–4·0	10	1·0–1·6	1·3	13·6–16·5	15·1

The results of earlier investigators are high because their cotton fibres included sand and dust, or had not been scrupulously cleaned first; if this is done the ash seldom exceeds 1·5%. The ash alkalinity shows that the mineral substances in the fibre are chiefly salts of organic acids; small quantities of chlorides, phosphates and sulphates, of potassium, sodium, calcium and magnesium, and smaller quantities of aluminium, iron and copper are present.

Copper Number.—The copper number of a cellulose material is defined as the weight in grams of copper reduced by 100 g. of the sample from the cupric to the cuprous state under standardised conditions. It measures the content of reducing constituents consisting of glucose and other sugar-like substances. Any one type of cotton gives a range of values of copper number, and the ranges for different types overlap. Clibbens and Geake [38] give the following mean values of copper number for various raw cottons :—

American : Long staple Upland 0·68 ; Georgia 0·97 ; Texas 1·09.

Egyptian : Uppers 0·93 ; Sakellaridis 1·04.

Indian : Bengal 1·54 ; Oomra 1·67 ; Surtee 2·28 ; Broach 2·97.

Peruvian : Tanguis 0·77 ; Smooth Peruvian 1·60.

Brazilian : Pernams 1·31 ; Ceara 1·37.

Mercerisation.—When cotton is immersed in 18% solution of caustic soda, the cellulose swells and fills out its cuticular covering so that the flattened twisted tube, characteristic of cotton, is transformed into a simple unconvoluted cylinder with little if any central canal. This transformation was discovered by John Mercer in 1844, and his name has since been given to the phenomenon. Practical use of it followed the discovery by Horace Lowe in 1890, that if the transformation was carried out on yarn or cloth under tension, the material became highly lustrous. The material is either kept in a state of tension throughout the operation, or is allowed to shrink in the alkaline liquid and afterwards stretched to its original length and kept so while the alkali is washed out. Corser and Turner[39] have shown that the changes that take place in the yarn depend on the degree of twist; in commercial practice two-fold yarns are commonly used of a low twist, and such yarns show a large increase in strength after mercerisation (*v.* FINISHING OF TEXTILE FABRICS, this Vol., p. 184).

When cotton is treated with a mixture of nitric and sulphuric acids, it is converted into nitro-cellulose or gun-cotton (*v.* EXPLOSIVES). By dissolving gun-cotton in a mixture of ether and alcohol, collodion is obtained (*v.* CELLULOSE LACQUERS Vol. II, 468*c*). Nitro-cellulose is also used with camphor to make "*celluloid*" (*q.v.*). When treated with acetic anhydride in glacial acetic acid solution, in the presence of a small quantity of sulphuric acid or other catalyst, cotton yields "*cellulose acetate*" (*v.* CELLULOSE Vol. II, 464*d*,), used among other things for making a synthetic textile fibre. Cotton also dissolves in cuprammonium (ammoniacal cupric hydroxide), a solution also used for making a synthetic textile fibre (*v.* FIBRES, ARTIFICIAL).

Cotton Technology.

12. COTTON GINNING AND PRESSING.[40]—Ginning consists of the separation of the lint from the seed. There are two chief types—roller gins and saw gins. The roller gin consists of leather discs mounted on a wooden roller; the leather roller turns against a "doctor" knife, the fibres cling to the leather roller and pass between it and the doctor knife, and the seeds being unable to follow, are detached. The lint is automatically stripped on the opposite side of the roller by means of a bar. This gin is particularly suitable for long staple cottons, and small seeded cottons, and accordingly finds a use in nearly all cotton-growing countries. The chief objection to its use is its low rate of production, being only up to 80 lb. lint per hour even for the most up-to-date types. The saw gin is particularly suitable for the large seeded American type of cotton ; in this gin from 70 to 80 circular saws (10 in. to 12 in. diameter), mounted on a central shaft, pass between steel ribs with only small clearance on either side ; the seed cotton is fed from above, the lint is seized by the teeth of the saws, the seeds cannot pass through the gaps between the ribs and are accordingly detached. Much care is necessary to ensure that no damage is done to the fibre by the vigorous action of the saw teeth. The lint is stripped from the saw teeth on the opposite side of the machine either by a brush action or by pneumatic means. Whereas the roller gins work individually,

modern saw gins are run in batteries of four, the seed cotton being sucked pneumatically from the country cart direct to feed the gin, and the separated lint delivered pneumatically from the gins direct to the press. The production of a saw gin is up to 400 lb. lint per hour. Saw-ginned cotton taken from a bale has quite a different appearance from roller-ginned cotton, besides being generally cleaner, owing to cleaning operations being readily possible with the pneumatic conveying methods employed.

The ginned cotton is made into bales in presses; usually in two stages—first to low compression bales (density about 10 lb. per cu. ft.) and then to high compression bales (density 30–50 lb. per cu. ft.). In U.S.A. and Egypt the low compression bales are made at the ginneries, the high compression bales at compress stations in U.S.A. and at Alexandria in Egypt. High compression saves transport costs, but adds to difficulties in spinning mills.

13. COTTON SPINNING.[40]—The processes of cotton spinning derive from the qualities desired in yarns, viz. (1) a certain fineness or *counts*, indicated by the number of hanks, each 840 yards long, that are needed to weigh 1 lb.; (2) strength; (3) levelness; (4) appearance—freedom from neps, or blobs of rolled-up cotton fibres, and from foreign matter (small particles of leaf, bract, stem, seed-coat, etc.). All these qualities are borne in mind throughout the various stages of processing that are necessary, but they are attained roughly in the reverse order to that given.

The highly compressed bales have to be opened up (1) to separate off the foreign matter disseminated throughout the bale, and (2) to separate the individual fibres so as to facilitate their proper arrangement and to achieve regularity and strength.

The chief divisions in a typical cotton spinning mill besides the office are :—

(1) Cotton room; (2) mixing room; (3) blowing room, for opening and cleaning the cotton; (4) cardroom, for carding, drawing, combing the cotton and forming roving; (5) spinning room; (6) preparation room; (7) cellar for "conditioning" the yarn, storing, etc.

Opening and Cleaning.—The high pressure used in forming the bales gives them a stratified form; in the spinning mill, sheets of this bale cotton are peeled off by hand and fed to a hopper bale breaker, Fig. 2; this machine has a rising spiked lattice slightly inclined to the vertical which takes the cotton up past a device that allows part only of the cotton to go forward, to be penetrated by spikes and struck by leather flaps, and then delivered as large lumps. These large lumps are often transported by travelling lattices, or pneumatically through trunks, to the mixing room, where stacks are built up in horizontal strata of different "marks" of cotton, from which the cotton is removed uniformly from a vertical face so as to include the desired proportions of the different "marks." In many mills, especially those engaged in making the coarser and cheaper types of yarn, economy is secured by omitting the mixing room and making the mixing direct at the bale breaker, passing the cotton thence straight to the blowing room, so called because in this room the cotton is drawn through a number of machines by means of strong air currents developed by powerful fans.

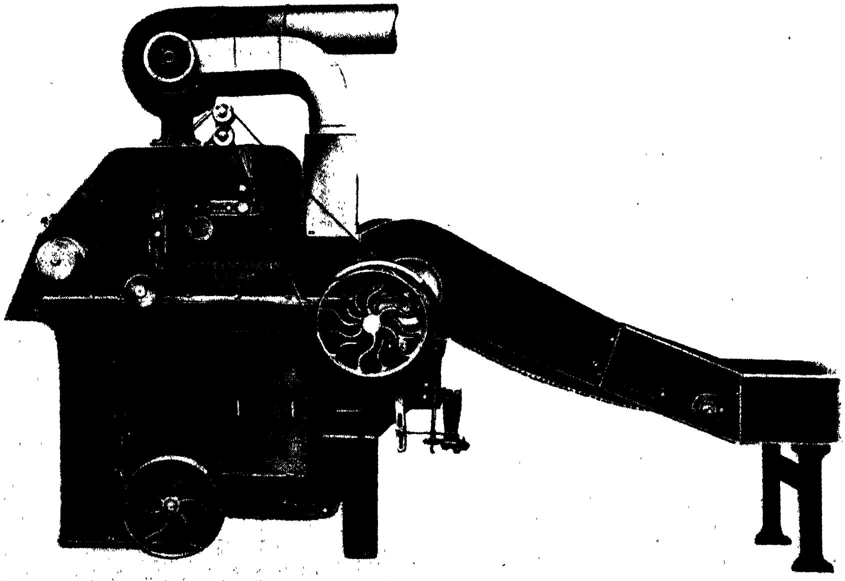

FIG. 2.—HOPPER OPENER.

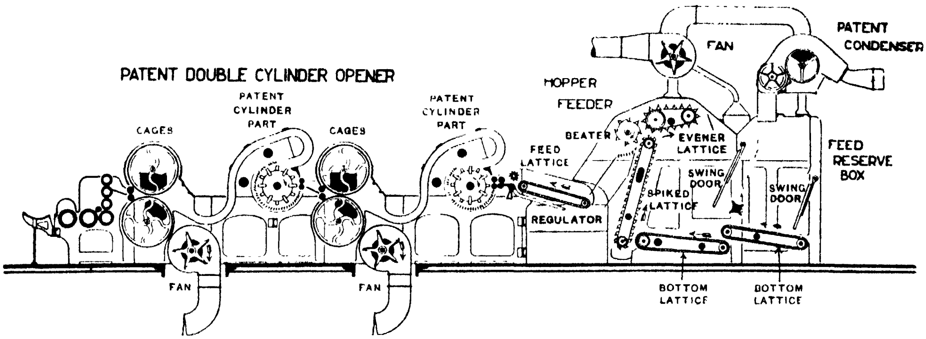

FIG. 3.—PATENT DOUBLE CYLINDER OPENER AND LAP MACHINE FED BY HOPPER FEEDER WITH FEED RESERVE BOX AND CONDENSER ATTACHED.

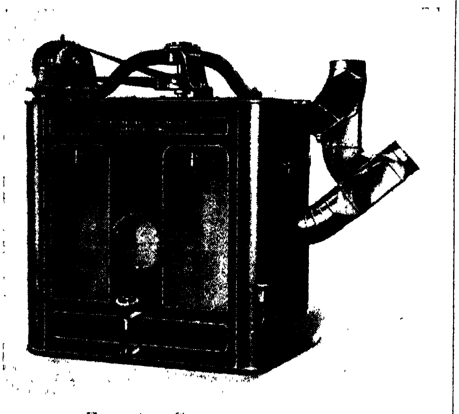

FIG. 4.—CRIGHTON OPENER.

The large lumps of cotton from the bale breakers or the mixing room are fed by means of hopper feeders, similar in principle to hopper bale breakers, to " porcupine," Fig. 3, and other opening machines equipped with a variety of beaters of a vigorous kind, heavy and swiftly revolving; beaters of various sizes, 41 in., 24 in. or 18 in. diameter with central horizontal shafts fitted with numerous iron discs to the periphery of which steel striking blades are attached at close intervals, revolving at 750 r.p.m. inside iron cylinders, break up the lumps to tufts. Another favourite type is the Crighton opener, Fig. 4, which has a vertical shaft with similar discs attached but increasing in diameter from the bottom to the top of the shaft; the spaces between the beater bars, which are slightly inclined to the vertical and surround the beater in the form of a truncated cone, provide a means of egress for the foreign matter. In its passage from one type of opening machine to another, the partly opened cotton is drawn pneumatically through trunking to specially shaped dust trunks, where more dust separates. Suitably placed fans draw the cotton through the various machines and often on to slowly revolving perforated or wire cages, through which the air passes, leaving the cotton on the surface of the cages ready for passing through a series of heavy calender rollers, forming part of the " lap end " where the cotton is formed into a " lap," a sort of thick but very soft sheet of felt rolled round a tube from which it is removed for feeding to the next machine, the scutcher, Fig. 5. At some point in the opening system the introduction of the fast revolving Shirley cage has recently found favour (see Fig. 3); this cage, moving at some 60–80 r.p.m., passes on the cotton so quickly that at any one time it is covered with only a comparatively thin fleece of cotton, through which fine dust can be drawn by the fan; in slow moving cages the cotton lies much too thickly on the cages for cleaning to occur at this point. The scutcher also is a kind of opening machine, distinguished particularly by the means which it offers of obtaining some degree of regularity in the product. Four laps are unrolled on a lattice so as to flow one above the other to feed rollers that deliver a fringe to be struck by a rapidly revolving beater, sometimes of the porcupine or bladed-disc type used in many openers, but more often of the bladed type, consisting of two (sometimes three) steel blades, carried by steel arms parallel to but some inches distant from the shaft, which revolves at 800–1,200 r.p.m. The superposition of the four laps to secure regularity is a simple device; a thick place in one lap may be neutralised by a thin place in one of the others; at the worst, thick (or thin) places may come together in all four laps, in which case the *relative* irregularity at this place is unchanged, but the chances of this occurring are obviously small. Another device, the " regulator," is attached to the feed rollers, which automatically slow down if the average thickness passing through them is above the predetermined normal, and speed up if this average thickness is below normal. By this means the weight per unit length of the lap is kept normal within limits. An ordinary line of opening machines will open up to 40,000 lb. cotton per week, a finisher scutcher up to 20,000 lb. per week, so usually there are two scutchers served by each line of opening machinery.

In recent years attempts have been made to economise in the blowing room, and to avoid the heavy pressing of the cotton at the " lap ends," as this is held to defeat the very purpose of opening. For this purpose " single process opening " has been developed ; a series of hopper feeders and openers is linked together, with electrical devices to control the passage of the cotton through the various units, so that baled cotton is fed at one end and laps are made at the other, with no handling of the material in between. It is claimed that productions up to 40,000 lb. per week and above are possible with a single line of such machines, and that the very serious irregularities arising from human lapses are avoided by its introduction.

Working along quite different lines, the British Cotton Industry Research Association has introduced the " Pneuopener," an opening machine on the lines of the " Shirley Analyser " in which a taker-in type of beater (*see Carding, below*) of 15½ in. diameter, revolving at 1,600 r.p.m., opens to a very high degree the cotton prepared on an ordinary type of opener, and by placing it in a streamlined air-flow accomplishes the separation of the lint from the foreign matter. Combination machines on the same principle are in prospect.

The exact blowing-room treatment given to a cotton depends on the type of cotton, the degree to which it is compressed, and the amount of foreign matter it contains. Though the severe beating the cotton receives is not so detrimental to the fibres as might be supposed, yet the general practice is to give as little beating as will serve the purpose in view—in short, the extent of the treatment is what is necessary and sufficient. As a consequence, there is far more variety among the blowing rooms of mills than in any other section.

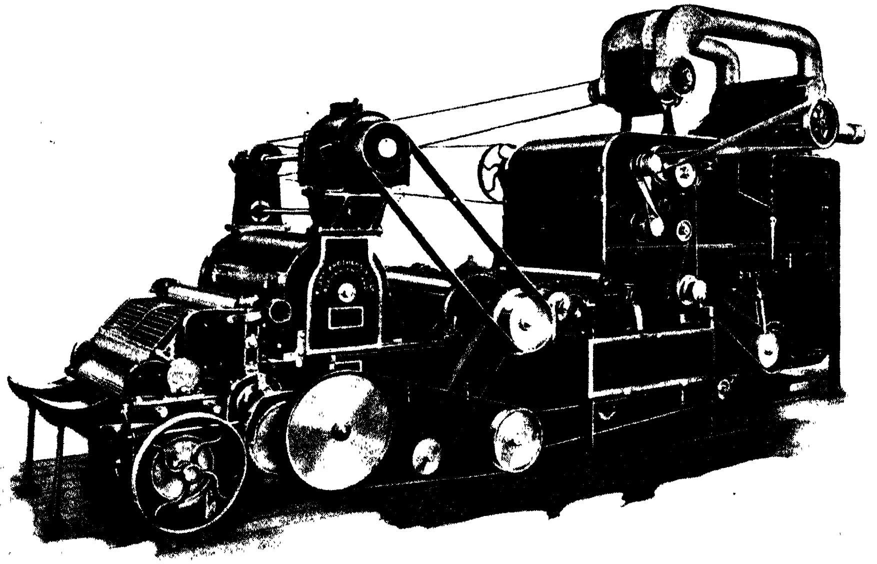

FIG. 5.—SINGLE SCUTCHER AND LAP MACHINE, FED BY HOPPER FEEDER.

Cardroom Processes.—The cardroom processes are, with one or two very important exceptions, much less drastic in their action on the cotton than the blowing-room processes ; the exceptions are carding proper, and combing ; these two processes complete the final separation of the fibres from one another, which thereby run grave risk of breakage.

Carding.—The laps from the scutcher consist of tufts of cotton still containing an appreciable quantity of foreign matter (*trash*). It is the function of the carding engine, Figs. 6 and 7, to disentangle the fibres of each tuft from one another, and to remove the remaining trash.

Carding proper consists in passing the tufts between two carding surfaces, *i.e.* surfaces covered with numerous fine wires set at an angle, with their points opposed to one another. A tuft of cotton between two such surfaces moving in opposite directions may be quickly disentangled and the fibres separated from one another. Before the carding itself is done, however, a final cleaning action is carried out by means of a taker-in feed.

As the lap unrolls it passes between a feed roller and a specially shaped feed plate, and is then acted on by the saw-like teeth of the " taker-in "—a cylinder (9 in. diameter) covered with wire set spirally in its surface to give 8 rows per inch width, with 4 teeth per inch along the wire. The taker-in revolves at some 400 r.p.m. ; cotton on its teeth passes one or two " mote knives " which help to remove trash, thence over the taker-in grid, to be transferred to the main cylinder, 50 in. diameter, moving at 160 r.p.m., and covered with card wire, *i.e.*

tempered steel wire set at an angle, with a density of 500 to 750 points per square inch. The second carding surface normally consists of a chain of over 100 " flats "—individual carding surfaces extending over the width of the carding engine (*e.g.* 45 in.) and only 1 in. in a fore and aft direction. These flats revolve slowly to facilitate cleaning, each flat being in position for carding for about 20 minutes; some 46 flats are engaged in carding at any instant. The two carding surfaces are set very close together (0·007 in.) and complete the separation of the fibres. The cotton emerging from between the carding surfaces passes on to a slow-moving card-wire covered cylinder, the " doffer," 26 in. diameter, from which it is stripped by a fast-oscillating " doffer comb "; the doffer web thus obtained is passed through a

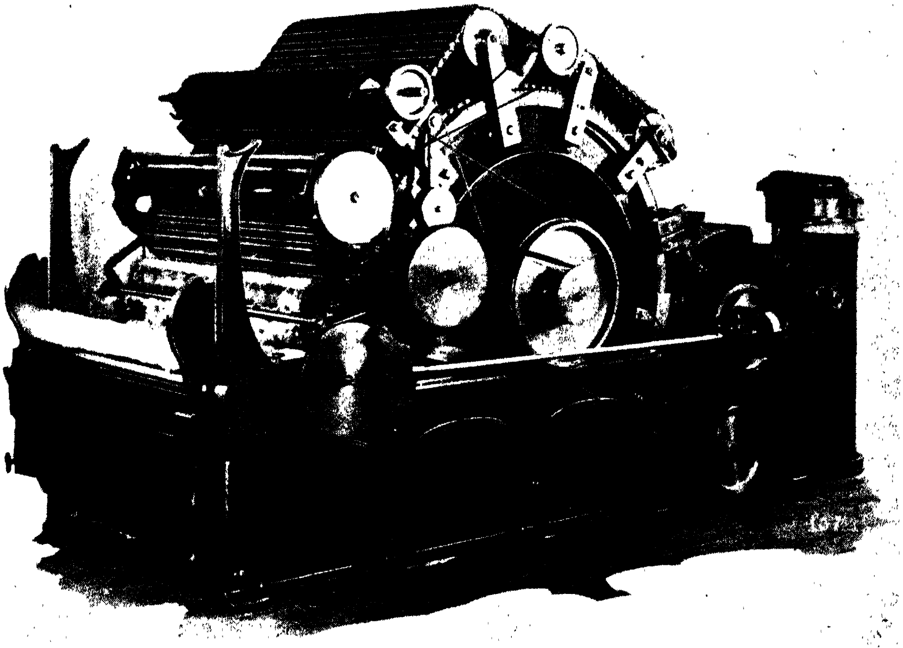

FIG. 6.—REVOLVING FLAT CARDING ENGINE.

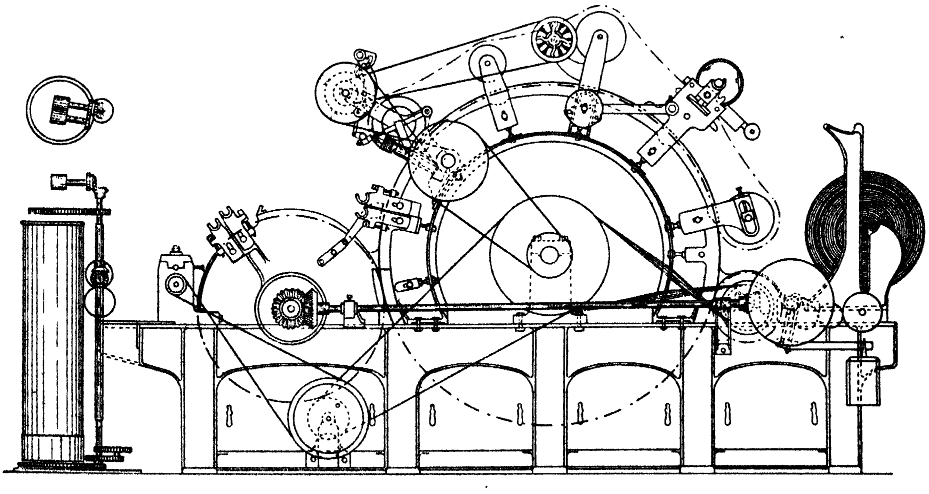

FIG. 7.—REVOLVING FLAT CARDING ENGINE: SECTIONAL ELEVATION.

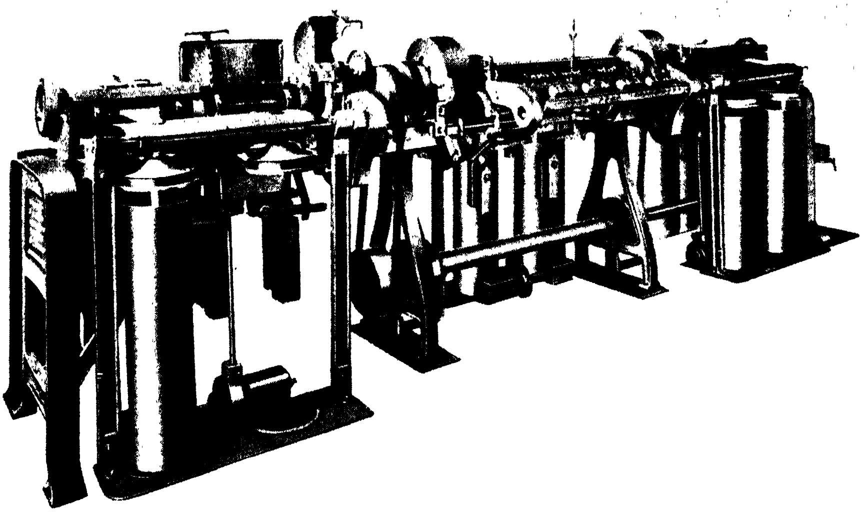

FIG. 8.—DRAWING FRAME.

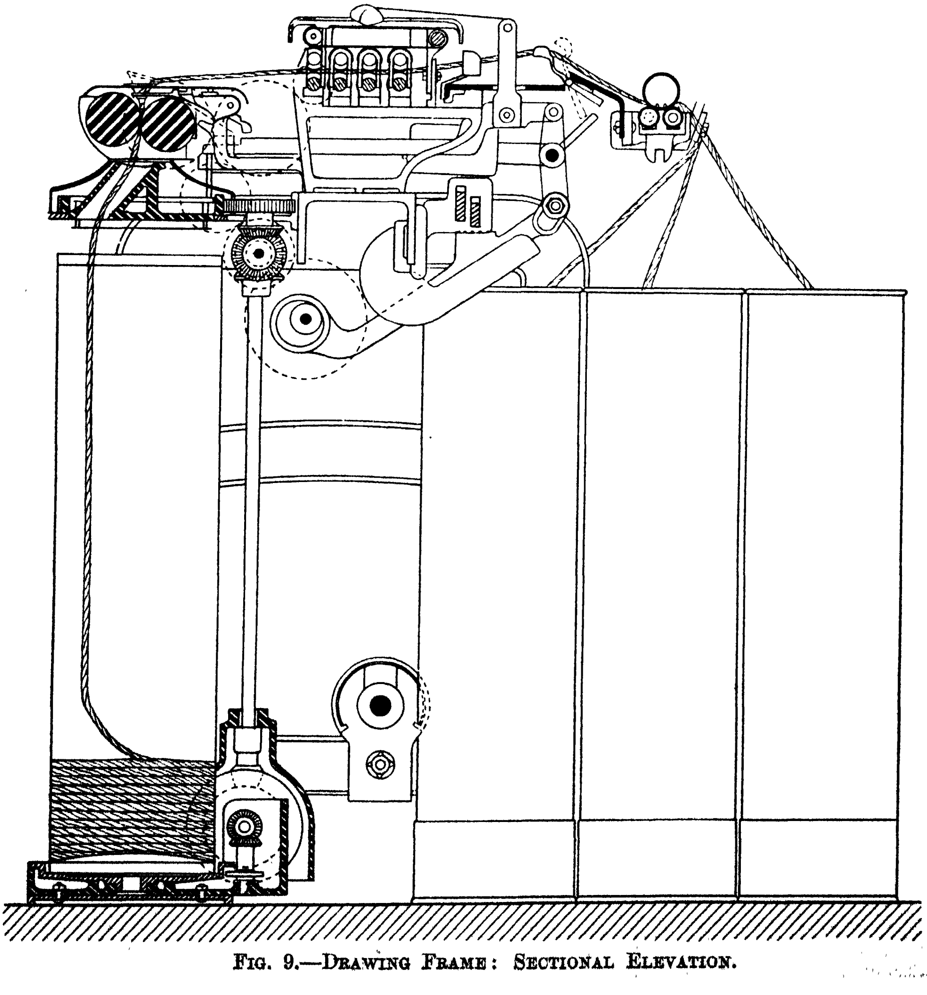

FIG. 9.—DRAWING FRAME: SECTIONAL ELEVATION.

pair of calender rollers and collected in a coiling can as a "sliver," a continuous rope of fibres which adhere together almost entirely by their natural clinging powers.

Combing.—Superior cottons are often combed; this operation is done on the card slivers, which are combined together to make first a "sliver lap" and then a "ribbon lap," by a combination and drawing out of sliver laps; through the end of the ribbon lap a series of 17 or 20 combs of gradually increasing fineness is passed; the combed figure is drawn out from the end of the lap, the new fringe combed, drawn out and pieced up with the fibres previously drawn out, and so on, the repetition of the cycle giving rise to a sheet of combed fibres which are then condensed to form the "combed sliver." This operation is valuable in removing short fibres, particularly neps; it also serves to place the fibres in a parallel condition a condition conducive to strength of yarn.

Drawing.—To increase the regularity of the sliver, and in the case of card sliver, also to make the fibres more nearly parallel, six or eight card or combed slivers are passed together, alongside one another, through four pairs of weighted rollers, each successive pair revolving more quickly than the preceding pair, and so drawing out the material, the "drafts" being so arranged that the emerging material has nearly the same weight per unit length as one of the slivers fed. This treatment through "one head of drawing" is repeated—two, three and occasionally even four heads of drawing being given, Figs. 8 and 9.

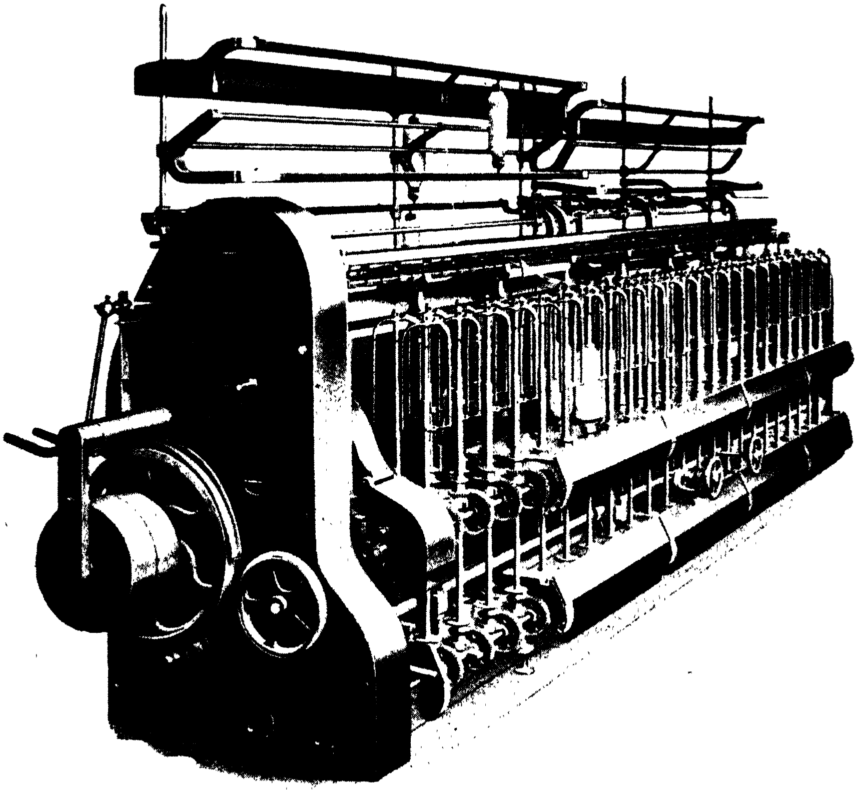

FIG. 10.—INTERMEDIATE ROVING FRAME (46 SPINDLES).
A full-size roving frame may have 160 or more spindles.

Speed Frames.—The sliver from the draw-frames is the most regular product in the cotton spinning mill. The function of the succeeding machines is to reduce the number of fibres in the cross-section, usually in successive stages, prior to the completion of the spinning processes by the insertion of twist to give strength at the final stage of attenuation. These successive stages are carried out on the speed (flyer) frames—the slubbing, intermediate, roving, Fig. 10, and also the jack frame for very fine yarns; the product of each of these machines is known by the name of the corresponding machine. The drafting principle employed is the same as that of the drawing frames, the material passing between three lines (pairs) of rollers revolving at increasing surface speeds. Much effort has been devoted in recent years to economising in the process of attenuation, with a certain amount of success. Except in fine spinning, it is not usual to use drafts higher than 6, but in these "high draft" systems the draft may be 20 or 30 or more. Such systems depend for their success on better fibre-control during drafting operations. For convenience of handling, the attenuated products are given a slight twist and wound on to a bobbin—processes which give rise to complicated mechanical problems but have no detrimental effect on the material.

Spinning.—The spinning machine proper is the final machine used in the formation of the yarn, and inserts the desired amount of twist in the roving, after its further attenuation in the spinning machine itself. There are two methods for inserting the twist. The first is by means of the *mule*, Fig. 11; this has a carriage which moves in and out about 5 ft., and which carries many slender spindles, revolving at speeds up to 12,000 r.p.m. Rovings are placed in a fixed creel, and led to the spindles through 3 lines of drafting rollers; as the carriage moves outwards roving is delivered by the rollers and the revolving spindles insert twist to the desired amount; the carriage then moves inwards, and the spindles revolve more slowly and wind up the spun yarn. Twisting and winding are thus consecutive and the spinning process is intermittent; the carriage makes a complete in-and-out movement about four times per minute. The mechanical control is such that the tension during twisting and winding is controlled to a nicety, making possible the spinning of soft, full yarns desired for weft, as well as very fine yarns having rather low strength. For these reasons the mule has for a long time held its ground fairly well as a means of cotton spinning against the developments of its formidable rival—the *ring frame*, Fig. 12. This takes its name from the flanged steel rings that encircle wooden bobbins or paper tubes mounted on spindles that revolve at speeds up to 10,000 r.p.m.; on the flange of each ring is sprung a small piece of steel wire called a "traveller," through which the drawn-out roving passes on its way from the drafting rollers to the bobbins. The revolution of the bobbin creates a tension in the yarn which drags the traveller round the ring at a slightly slower speed of revolution than that of the bobbin itself; the difference between the two rates of revolution represents the number of coils of yarn wound on to the bobbin. Thus on the ring frame twisting and winding proceed simultaneously and continuously. Owing to the tension inseparable from the method of spinning, ring spinning is not suitable for very fine or very weak yarns. The same reason makes it necessary to wind the yarn on a much larger diameter on a ring spindle than on a mule spindle, with the consequence that for a given weight of yarn the ring spindle gives a much bulkier package than the mule.

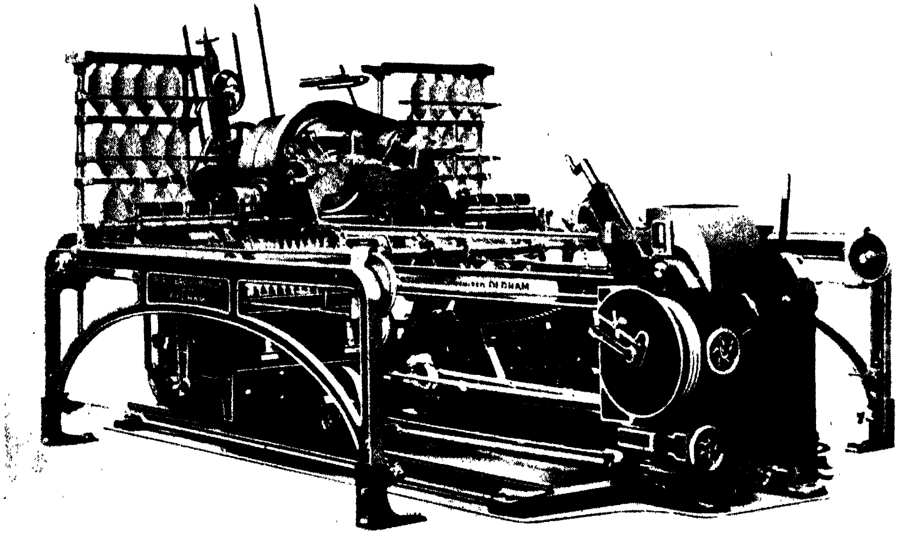

FIG. 11.—SELF-ACTING COTTON MULE.
Headstock with 24 spindles. (A full-size mule may have 1000 or more spindles.)

It may be noted that the twist inserted in a yarn may be clockwise or anti-clockwise, indicated respectively by the slope of the middle of the letters S and Z, these also being known as weft way twist and twist way twist. Z-twist is generally used for warp yarns—commonly known as "twist"—and also for the rovings made in the cardroom; S-twist is generally used for weft.

The amount of twist inserted depends on the purpose for which the yarn is intended; fine yarns require more twist than coarser ones, and the actual turns of twist per inch are obtained by multiplying the square root of the counts by a certain twist factor; common twist-factors are 3·17 for mule weft, 3·75 for mule twist, and 4·0 for ring twist; for "doubling weft," *i.e.* yarn intended for doubling and actually spun with Z-twist, the twist-factor is 2·9 or less.

Cotton Doubling and Twisting.[41]—A large proportion of coarse and medium cotton yarns is used for making fabrics in the form of "singles," *i.e.* as spun, but with some suitable preparation; the remainder, and about 75% of fine yarn, are used in the folded state, *i.e.* two or more single yarns are twisted together to form a "thread." Such folded yarns have a multitude of uses; *e.g.* they are used directly as threads for sewing, crochet, embroidery; in making hosiery, nettings, lace; and in woven fabrics such as canvases, ducks, voiles, poplins. The machines generally used for making such threads are the "twiner" and "ring doubler" which are very similar in principle to the mule and ring frame respectively, the chief difference being that their feed rollers do no drafting.

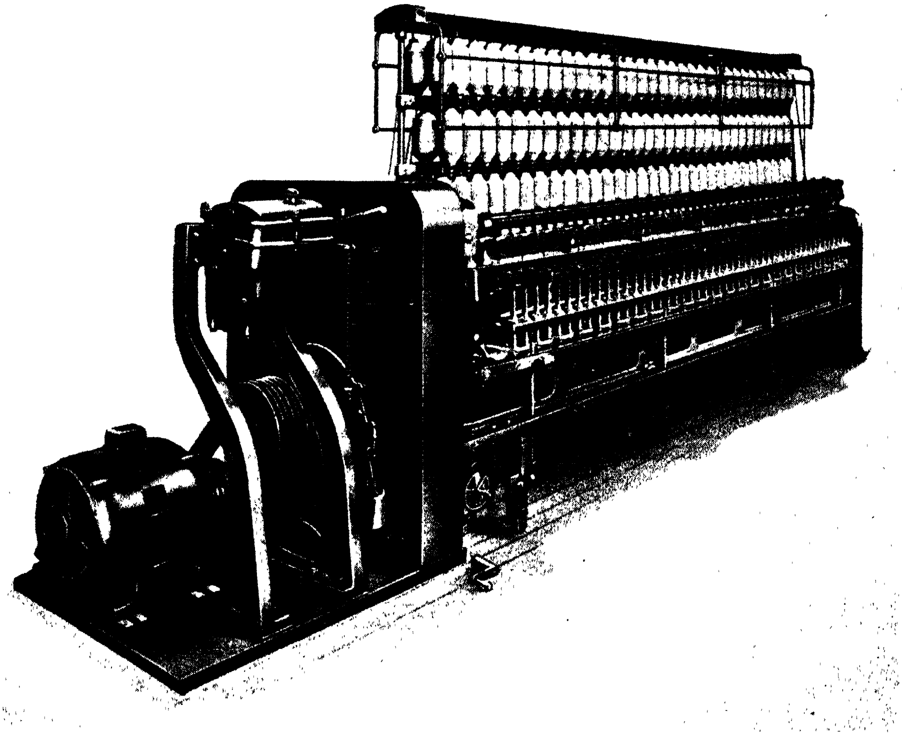

FIG. 12.—RING SPINNING FRAME (48 SPINDLES).
A full-size ring frame may have 400 or more spindles.

14. COTTON YARN PREPARATION.*—Before the yarns spun on mule or ring frame can be woven into cloth, certain preparatory processes are necessary for weaving. Cloth is woven in a loom by the interlacing of two sets of yarns at right angles to each other; those passing from side to side of the cloth are weft yarns, and those that lie lengthwise in the cloth are warp yarns. The yarns made by the spinner from raw cotton are known as "grey yarns," and if made into cloth without undergoing bleaching or dyeing, they form "grey cloth," the actual colour of which depends on the colour of the cotton used, and ranges from dull white to various fawn shades. Often, however, striped cloths are made from yarns that have to be bleached, dyed or mercerised before being placed in the loom. Thus the preparation needed for yarn depends on (1) whether it is in the form of mule cops or ring bobbins (or tubes); (2) whether it is needed for warp or weft; and (3) whether it is to be

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* It should be noted that once the yarn has been spun, the subsequent processes tend to be alike, no matter what may be the fibre of which the yarn is composed. There is still great variety in the subsequent methods of processing; but the choice of a particular method is guided by consideration of many factors, of which the properties of the fibre itself constitute only one, whereas in the spinning processes these determine almost entirely the processing and machinery used. The machinery used for cotton doubling and weaving can in fact be used with comparatively slight modification for the doubling and weaving of similar yarns made from other fibres.

used grey or coloured. These three considerations govern the choice of the preparatory processes—the choice in every case being decided on economic grounds relative to the means available. Mule weft cops are very compact and suitable for immediate insertion in the shuttle of a loom; ring bobbins, pirns or tubes may be made small for this purpose, but then need frequent replenishing, which may be accomplished on an automatic loom without difficulty, but otherwise may be expensive in labour costs. For some purposes mule weft may be re-wound on a high-speed winding frame into a more compact package, though whether the cost of re-winding is recouped depends upon the actual yarns used and the cloths being woven. Warp yarns—even grey warps—require much more preparation than weft.

In a fine cloth there may be 3,000 or more individual warp yarns, and in weaving, the breakage of a single yarn requires the stoppage of the loom for its repair, a comparatively lengthy operation; such stoppages are minimised by breaking out the weakest places in a winding frame, in which the yarn from mule or ring twist is wound on to double flanged "warper's bobbins" carried on vertical spindles. As each yarn proceeds independently in this operation, the breakage of any one yarn under the tension of winding merely results in the cessation of winding on a single spindle. There are further economic reasons for "winding" the warp yarns. Many fabrics are of a standard type, of which many thousand yards are required; and before the warp is ready for weaving in the loom it has to receive a coating of "size" (v. 15. SIZING), be wound on a "beam" (*see below*), and the individual yarns drawn in proper order through "healds" carried on two or more "shafts" or "staves" and then through the "reed." As each yarn has to be handled separately in these processes they are tedious and expensive, but require to be done only once for each warp; thus economy is secured by making the warp as long as possible. A single warper's bobbin holds 8 oz. or more of yarn, or over 13,000 yards of 32's count.

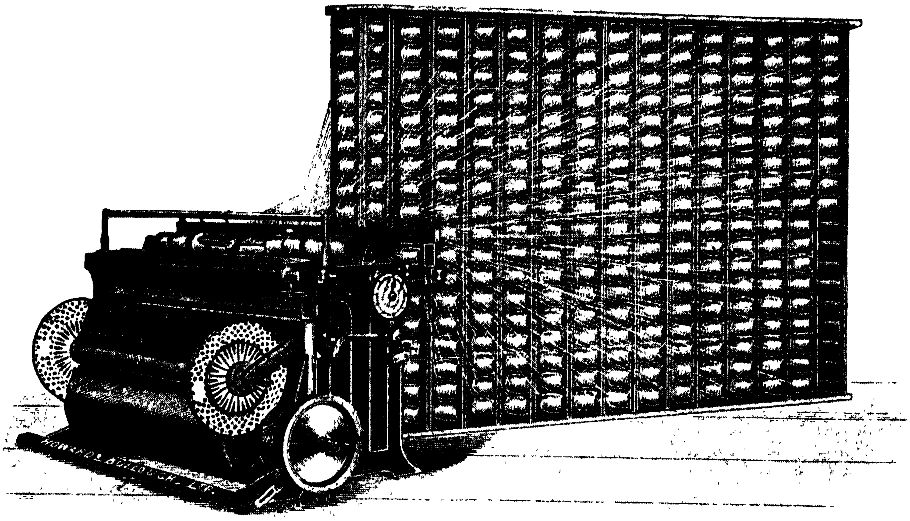
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FIG. 13.—BEAM WARPER.

For a cloth containing up to 2,000 warp threads (ends) of 32's yarn, the first stage is to make 4 beams each containing 500 ends, on a *beaming frame*, Fig. 13. This consists of a creel, or framework, on which 500 warper's bobbins are placed; the threads are led from these through a reed, over and under certain rollers, through drop-wires or pins (they resemble hair-pins), one on each thread, then through an expanding comb, over a small roller to a "beam"—a wooden roller with large iron-flanged ends. The beam rests on a large wooden drum which is power-driven and in revolving causes the beam also to revolve and wind on the 500 threads. The purpose of the pins is to detect broken threads, a breakage causing the pin to drop and the machine to stop. A self-stopping measuring motion, set beforehand, causes the frame to stop when the desired length has been wound on the beam. The four similar beams are placed at the rear of the *slasher sizer* or *tape sizing frame*; in this machine the threads are led forward to form a single sheet which is led beneath a roller immersed in boiling size contained within a shallow box. The threads then pass between squeezing rollers, and thence on to the surface of two large steam heated cylinders, for drying the yarns; on leaving the cylinders the yarns are separated from one another by means of dividing rods, and are then led through an expanding reed on to the weaver's beam. Details of "sizing" ingredients and their preparation are given below in section 15.

The beaming frame and the slasher sizer are the most economical means of preparing grey warps and warps of one colour. The method of preparation of other coloured warps largely depends on the length of the warp, the number of threads required, and the number of colours. When many weaver's beams are required all of the same pattern, the yarn is first wound into hanks, in which form it is bleached and/or dyed, and sized, then wound on to warper's bobbins; these are made first into beam warps and finally into loom warps. But when many colours are used, the warper's bobbins in the beaming frame are made into a "*sectional*" warp of narrow width, with all the threads in the same order as required on the weaver's beam; a number of these sections are placed alongside one another on a single beam, from which they are run off on to a weaver's beam. When only three or four colours are used, the warp is made on a large circular or other type of frame, from which it is made into a *ball* or *chain*, a convenient form for handling prior to dyeing and sizing. A number of such warps are combined and the threads placed in due order on a *Yorkshire dressing frame*; this process is a slow one because the separation of the threads from the different coloured warps and their arrangement in due order in a reed has to be done by hand before they can be wound on to the power-driven weaver's beam; during this winding, the warp is "dressed" by moving the reed to and fro, and brushing the warp before it reaches the reed. When long lengths of such warps are required in one pattern, the different coloured warps of 300 to 500 ends may be dressed separately on to back beams on a Yorkshire dressing frame, and the back beams run off and their four warps combined on to a weaver's beam in a further machine—the *Scotch dressing frame*.

The final stage of preparing the warp consists of drawing the ends through the healds and reed in their order. For this purpose the "beam" is mounted in a "drawing-in machine," and the drawer-in draws each individual thread in turn through its own appropriate heald and "dent," or space between two wires of the reed. Where the warp is followed by an exactly similar warp in the loom, much time is saved and the cost reduced by leaving threads of the old warp in the healds and reed, and merely twisting together the corresponding ends of the old and new warps. In recent years, mechanical methods have been introduced both for "drawing-in" and "twisting"—or "tying"—the warp, as these two operations are called.

15. SIZING.[34, 42]—Warp yarns are subjected to abrasion and high tension in weaving; coarse folded yarns for heavy cloths—ducks and canvases—can withstand the abrasion and tension without treatment, but single yarns have to receive a coating of "size" to reduce their liability to break in the loom. This "size" has a carbohydrate basis—either fermented flour, sago, maize (corn starch) or potato starch (farina); or sometimes vegetable gum. These when properly prepared act as adhesives which bind the outside fibres to the core of the yarn and prevent fraying during weaving. The film produced from any of these substances is harsh and brittle, and is therefore softened by adding tallow, which also acts as a lubricant, or some other softener—vegetable oil, wax, glycerin or soap. Other substances may also be added, *e.g.* china clay for weighting purposes; the deliquescent magnesium or calcium chlorides, or glycerin, to keep the yarn moist and pliable; and zinc chloride or "*Shirlan*" to prevent the yarn mildewing. For *light sizing*, used for poplins, shirtings, linings, etc.—or cloths that are bleached, printed or dyed, the size added amounts to 10–20% of the weight of the warp and consists almost entirely of sago or flour, with a little softener and antiseptic; for *medium sizing*, adding 20–50% to the weight of the warp, the extra weight is attained by the use of china clay; such sizing is used for Indian drills, China shirtings—coarse yarn cloths which are shipped in the grey state. *Heavy sizing* is intended for weighting purposes, and may add as much as 100% to the weight of the cloth formerly sold in the native markets abroad. Wheaten flour, fermented or steeped with zinc chloride, is largely used as the basis of this sizing, though for still heavier sizing gums may be added in conjunction with china clay as a weighting agent.

The different ingredients are prepared in a series of *becks* or large tanks of some 600 gallons capacity. For fermented flour, four such becks may be used, two for fermenting the flour and two for mixing and boiling; the becks are provided with agitators for stirring, and pumps for transferring the mixture from one beck to another; at the bottom of the mixing becks are perforated copper pipes to admit steam for heating. Making up a flour mixing for fermenting is spread over 3 or 4 days—some eight sacks of flour being added gradually with an appropriate amount of water, with continuous stirring; it is allowed to ferment for some weeks (2 to 6 or more) before use. For pure sizing for weaving, the mixing of 92% sago or wheat flour and 8% tallow would be suitable; the pure flour might be partly replaced by farina. For "50% medium sizing," a mixing used is: fermented flour 32%, china clay 15%, tallow 4%, magnesium chloride 1·25%, and zinc chloride 1%. For "100% heavy sizing": fermented flour 40%, china clay 40%, tallow 10%, magnesium chloride 5%, zinc chloride 4%. Although these recipes are mentioned, it must be realised that there is great variety in such recipes in sizing practice.

16. WEAVING.[43]—It has already been mentioned that weaving consists of the interlacing of two sets of threads—the weft and the warp—at right angles to each other. Success in commercial weaving is conditioned by the degree of control that can be exercised mechanically over the warp and the weft so as to permit of high-speed weaving; the gain from mechanisation in weaving is much less than in spinning, for while it has reduced spinning costs to about 1/40th, weaving costs in general have only been halved.

The machine for weaving is called a "loom." Looms vary in dimensions and construction to suit the different types of fabric woven on them

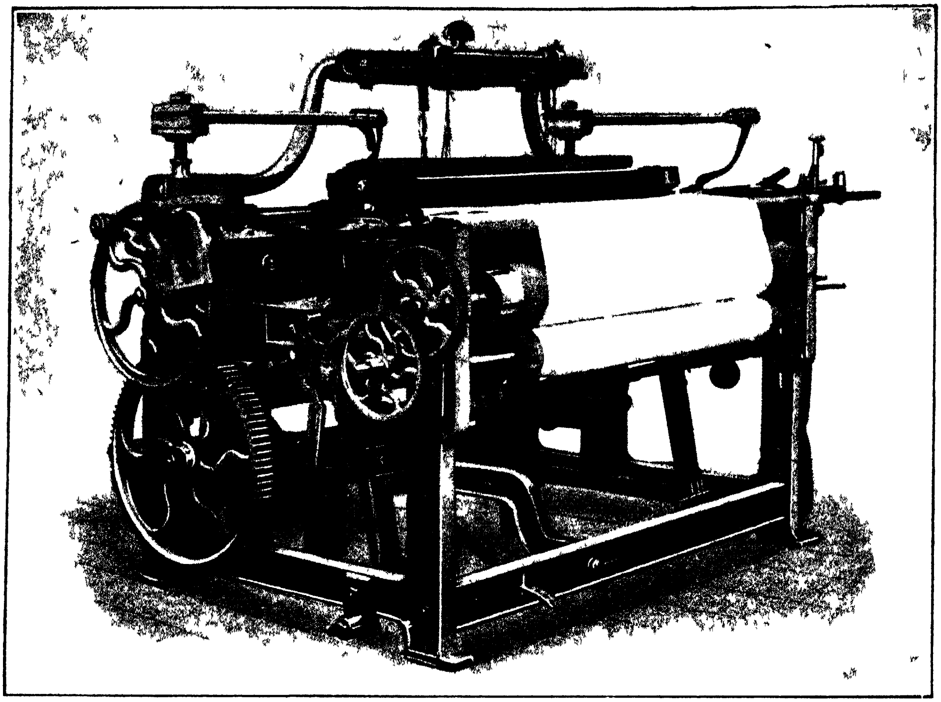


FIG. 14

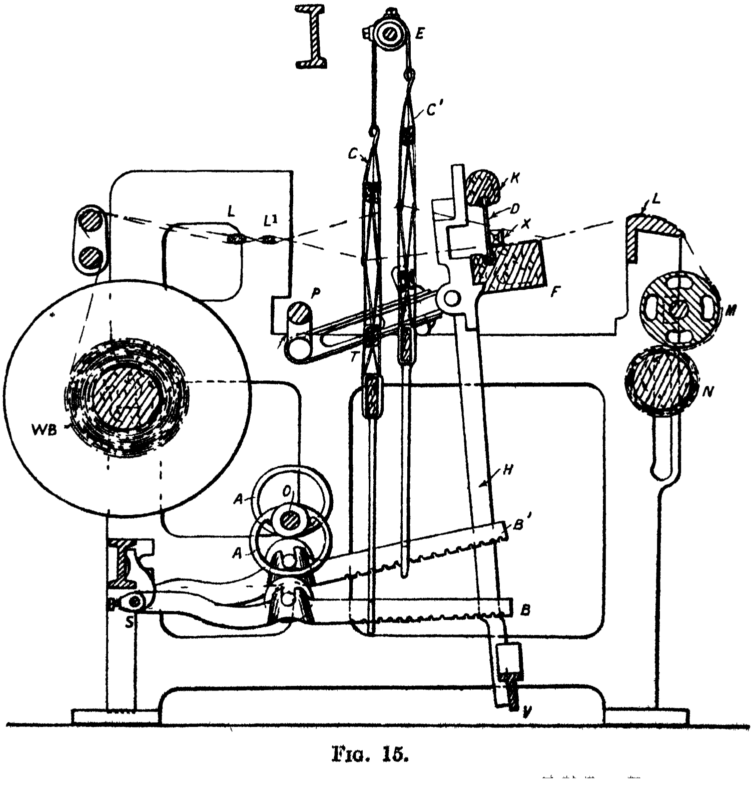


FIG. 15.

—of which the width, weight and design (if any) are the most important factors in this respect, as well as the fibre from which the yarns are made. The simplest type of loom is a *plain loom,* Figs. 14 and 15, used for making "plain cloth" such as calico, sheetings, etc., and in order to convey some idea of the process of weaving, the plain loom will be described in some detail.

Three primary operations are necessary to effect the interlacing of the threads:

(1) When the warp is unrolled from the beam to form a plane sheet, some of the warp threads must first be raised out of the plane; this operation is known as "*shedding.*"

(2) Through the shed formed by separating the warp into two planes, a weft thread or "pick" is passed; this operation is known as "*picking.*"

(3) The pick must be placed in its proper position relative to the previous pick; as this is not mechanically possible in picking itself, a separate operation known as "*beating up*" is necessary.

After one "pick" has been inserted a different "shed" is needed for the next "pick" in order to effect the interlacing, so some or all the warp threads must be moved relatively to each other, another pick inserted, beaten up, and the whole cycle repeated. For plain cloth only two types of shed are required, and these are formed alternately for successive picks. If we imagine all the warp threads to be numbered from one side, then in shedding, all the odd-numbered threads form one plane, and all the even-numbered threads form the second plane, and these two planes change places for successive picks. To effect this change of position, each warp thread passes through the eye of a "heald" (made of thick thread or wire, *see* Fig. 15), and all the healds controlling odd-numbered threads are mounted together on one "stave," and all those controlling even-numbered threads are mounted on a second stave. Thus the appropriate motions of the two staves determine which of the two sheds is formed. The relative disposition of the parts of a plain loom will be clear from the diagrammatic sketch, Fig. 15. The warp from the weaver's beam WB at the back of the loom passes over or under leese rods L, L′, and through the healds C, C′, which divide the warp and form the shed; the warp yarns continue to the fell of the cloth. The lower part of the shed rests on the race board of the slay F (a wooden beam); the shuttle X, is driven through the shed across the race board of the slay, leaving a trail of weft behind it; the weft thread is afterwards beaten up to the "fell" of the cloth by the reed D at the back of the slay. The cloth is drawn forward, as made, over the front rest L and the sand roller M, and thence to the cloth roller N, on which it is wound up; a special "taking up" mechanism governs the motion of the cloth roller and sand roller. This taking-up of the cloth necessitates a controlled unwinding of the weaver's beam by means of a "let-off" motion. The motion of the healds for shedding is accomplished by means of cords and straps from two levers B, B′ fulcrumed on a shaft S; cams (tappets) A, A′ on a bottom shaft move these tappet levers, the bottom shaft itself being driven from the crank shaft P, which is the main shaft of the loom driven by the external source of power. One pick is inserted during each revolution of the crank shaft; in plain weaving there are two sheds formed alternatively in a single revolution of the bottom shaft, during which two picks are inserted for every two revolutions of the crank shaft; and as the picking has to be done from each side of the loom alternately, the picking tappets to accomplish this are also mounted on the bottom shaft; each picking tappet acts on a conical picking bowl attached to a vertical picking shaft, on the top of which is fixed one end of a horizontal wooden picking arm; from the other end of the picking arm a leather strap, the picking band, passes to a buffalo hide "picker," which slides freely on a spindle in the "shuttle-box" and so drives the shuttle out of the box and across the shed each time each picking tappet operates —*i.e.* once each in every revolution of the bottom shaft; the two picking tappets on each side of the loom act alternately.

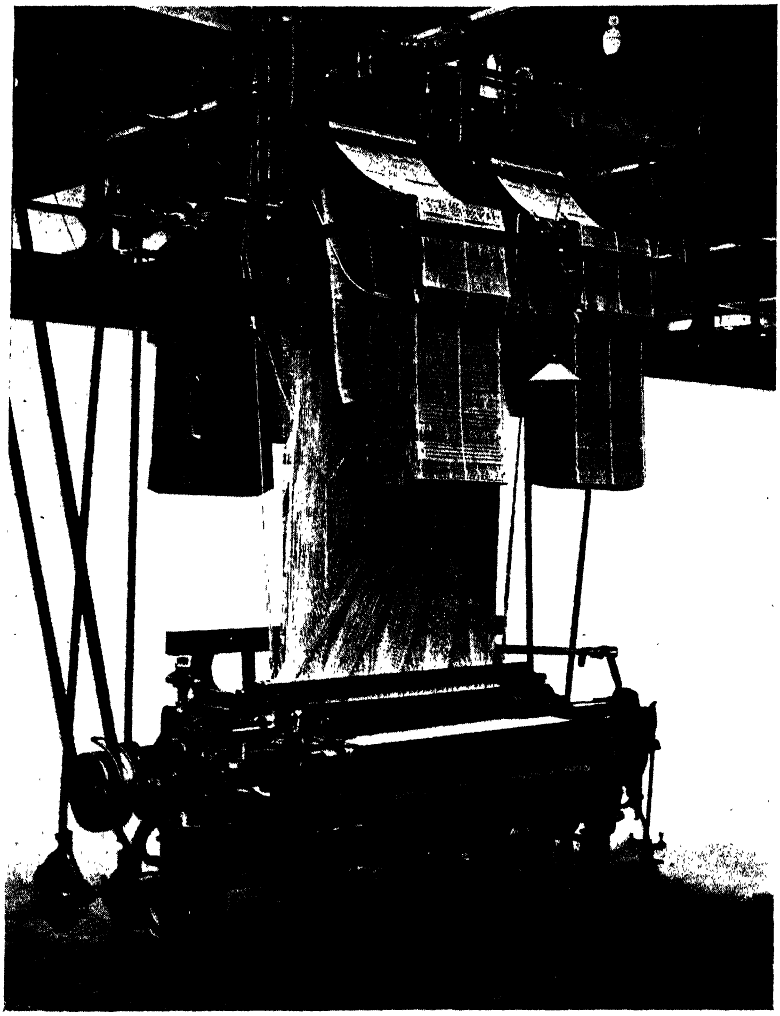
As beating up is necessary for every pick, the to-and-fro motion of the slay and reed is taken direct from the crank shaft by means of two cranks and connecting arms.

The slay itself is supported by two arms or swords, moving at their lower ends on rocking shafts. The speed of a loom is indicated by the number of picks inserted per minute; this number depends on various factors, such as the type of cloth being woven and the width of the loom; for looms making plain cloths 36 in. wide, the speed is some 200 picks per minute.

More complicated cloths than plain cloth are obtained by using more staves and varying the shedding. Any set of warp threads that move together to form part of the top shed or the bottom shed may be moved by one stave; but whereas for plain cloths and checks only two staves are essential, more are required for other cloths—up to 24 or above, according to the complication of the cloth. Tappets may still be used to actuate the shedding when comparatively simple cloth structures are required, such as drills, twills, satins, etc.; the limiting factor in the use of tappets is the number of sheddings necessary for each repeat of the pattern; for these cloths the tappets must be mounted on a countershaft during one revolution of which every type of interlacing in the repeat is effected. Thus for a simple satin made with 5 staves and repeating on 5 picks, the drive to the countershaft must be such that it revolves at only one-fifth of the speed of the crankshaft. There are many types of tappet looms, of varying capacity and arrangement of tappets.

The cost of weaving depends largely on the wages paid to the weavers; in Lancashire a weaver commonly attends to 4 looms only; such looms stop automatically at every few inches of cloth woven owing to the weft in the shuttle being used up. The weaver then has to withdraw the shuttle from the shuttle-box and replace it by another shuttle in which she has already placed a full cop, and re-start the loom. In a so-called "automatic loom" all these operations are performed automatically, without the loom stopping, through mechanism that acts on a battery of bobbins or shuttles at one side of the loom, and inserts a new bobbin or shuttle as required. With this relief a single weaver may attend as many as 20, 40, 60 or even more looms with considerable economy in total wages. This system has become very popular in America in the last 30 years, and is obviously eminently suitable where wage-rates are high and weavers scarce.

When the woven pattern is of greater complexity, consisting, for example, of diamonds, honeycombs, spots, or small figures, and requiring, say, 12–16 staves and repeating on 16 or more picks, the tappet method of shedding becomes unsuitable, and a machine called a *Dobby* is used for the purpose. This may be regarded as an attachment like a simple pianola, which causes the staves to be lifted by hooks which come into operation in accordance with the proper design set out by means of perforations in cards, or pegs in short wooden rods known as *lags*. The use of the dobby is restricted to small patterns because if the number of groups of warp threads that always move together exceeds 20, the number of staves required would correspondingly exceed 20—and this would make the weaving mechanically impossible owing to the space occupied by the staves and the necessity for all of them to give the same angle of shed in order to permit the free passage of the shuttle. Larger and more complicated woven patterns—characteristic of damasks, brocades, tapestries, quilts—are there-



[*Photo: Courtesy of Messrs. Butterworth and Dickinson.*

FIG. 16.—SIX-SHUTTLE REVOLVING BOX LOOM WITH DOUBLE JACQUARD MACHINE.

fore woven by means of a different machine—a *Jacquard*, Fig. 16, so called after its nominal inventor. In this machine provision is still made for groups of warp threads always to move together. What corresponds to a heald is made from a *mail* (7, Fig. 17) having a central eye through which the warp thread passes; twine is attached to the top and bottom of the mail, the lower twine carrying a slender leaden rod or *lingo* (8, Fig. 17) to act as a weight, whilst the upper twine is connected to a cord that passes vertically upwards through a hole in a board, the *comber board* (6, Fig. 17), and is then connected with the cords from all other mails which move together; a master cord—the neck cord (9, Fig. 17)—connects the junction of these cords with a hook on the Jacquard (4, Fig. 17); the combination of branching cords is known as the *harness*. The selection of mails by the Jacquard is similar to that of the dobby, perforated cards being used to determine the selection of mails to be raised; one card is needed for each pick, so that a pattern of many hundreds of picks requires as many cards; these are expensive in first cost, and in storage, and various inventions have aimed at reducing to a minimum the number of cards, and even reducing their size and weight, or at increasing the speed of the weaving. Jacquards are made in various sizes ranging from 100 to 600 hooks. The number of hooks represents the number of staves to which the Jacquard is equivalent, a common size being one of 400 hooks; while for large repeating patterns two machines, *e.g.* two 400's may be used (Fig. 16).

The action of a Jacquard is illustrated in Fig. 17. A horizontal wire needle with a loop at 1, passes through a perforated board 2 at one end, whilst the other end is looped and presses against a spiral spring 3; the loop 1 controls a vertical hook 4, which is bent as shown at its two ends, the lower end resting on the bottom board 10 when the hook is not lifted. A number of thin metal blades, on a frame, form a *griffe* 5, which is raised and lowered every pick; when the griffe is in its lower position the blades are about ¼ in. below the turned-over portion of the hook. If now the needle is pushed back, its loop moves the hook slightly aside, so that when the griffe rises its blade misses the turned-over top of the hook, and the hook does *not* rise, nor do the mails 7, which it controls; but if the needle is not pushed back, the griffe blade does catch in the top of the hook, which it lifts as it rises. The pushing back of the needles is effected by the perforated cards; for each pick one side of a square-section prism (the "cylinder") presses a card against the ends of all the needles; where holes have been punched in the card, the ends of the corresponding needles pass through the holes, and the hooks they control are not displaced, but are lifted by the griffe. Needles with no holes punched opposite to them in the card are pushed to one side, and the corresponding hooks are displaced and not lifted by the griffe, as shown for alternate hooks in Fig. 17. So the shed is formed and the pick inserted; the cycle is completed by the removal of the perforated card, when the spiral springs cause the needles to revert to their original

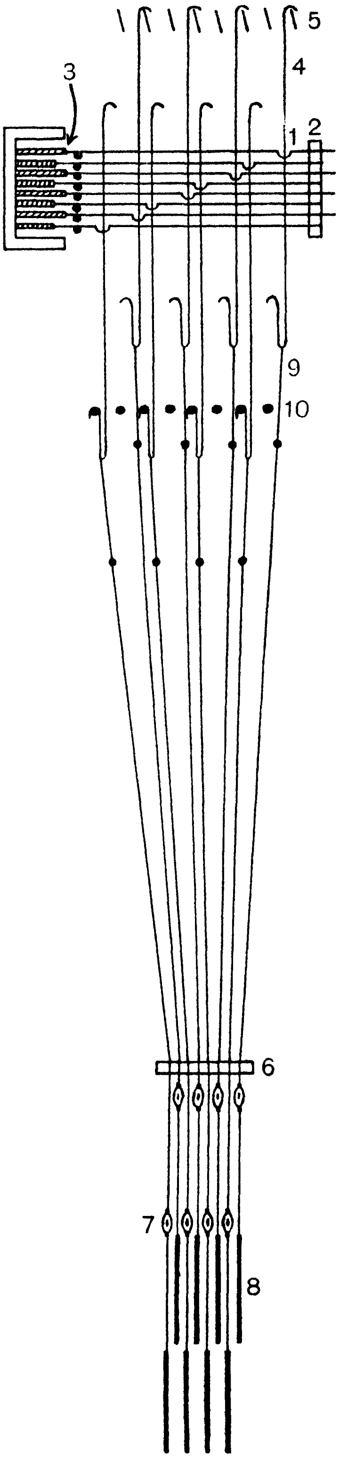


Fig. 17.—Action of a Jacquard.

positions, the griffe descends, and with it, by the action of the lingoes, the hooks that it lifted. Another cycle for the next pick then begins, the next perforated card being presented to the ends of the needles, the new shed is formed, the pick is inserted, and so the figure weaving proceeds.

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A. J. T.

FIBRES, VEGETABLE. *Classification.* Vegetable fibres are most satisfactorily classified according to the part of the plant from which they are derived. On this basis there are three groups, as follows:

(1) *Bast Fibres or Stem Fibres*, obtained from the fibrous strands which occur in the inner part (bast) of the cortex of the wand-like stems of certain dicotyledonous plants. These fibres are normally extracted by retting, followed by mechanical or hand treatment. Increasing attention is, however, being given to mechanical and chemical processes as alternatives to retting. Flax, hemp, jute, Bimlipatam jute, sunn hemp and ramie are the most important fibres of this class.

(2) *Leaf Fibres*, extracted from the leaves or leaf structures of monocotyledonous plants. The fibre is normally separated by purely mechanical processes involving the crushing of the leaf and the scraping of the leaf tissue from the fibre strands.

The chief leaf fibres of commerce are: Manila hemp, sisal, henequen, Phormium (New Zealand "flax"), Mauritius hemp, piassava and other brush-making fibres, and crin végétal.

(3) *Fibres from Seeds and Fruits.*—Cotton, a true seed hair, falls in this group, as also do the flosses, *e.g.* kapok (actually kapok fibres are attached to the capsule), simul and akund. As the seed hairs exist naturally in the free state, the separation of fibre from seed is all that is needed for their isolation.

Coir obtained from the fibrous husk of the coconut is another important member of this class of fibres.

Commercially, fibres are classed as "soft" or "hard," hard fibres being essentially cordage fibres. Since, however, the standard hard fibres are all leaf fibres, and the soft fibres all bast fibres, the botanical and the commercial classifications correspond.

Chemically, vegetable fibres are composed of cellulose associated with various amounts of lignin, pectinous substances, hemicelluloses, waxes, etc. From the analysis of a large number of different vegetable fibres, A. G. Norman (Biochem. J. 1936, **30**, 831; 1937, **31**, 1575) divides the common fibres into two broad groups on the basis of the xylan content of the cellulose in the fibre. The low-xylan group, with under 6% of xylan calculated on the cellulose, comprises the high quality textile fibres, whereas the fibres of coarser type, culminating in the hardwoods and straws, are found in the high-xylan group, 13–25%. None of the fibres examined yielded cellulose with between 6 and 13% of xylan. It was also established that the degree of lignification gave no indication of the type of cellulose to be met with.

The identification of vegetable fibres depends for the most part on certain colour reactions and on the dimensions and microscopic characteristics of the ultimate fibres, *i.e.* the elongated cells of which the fibre strands are built up. Reference should be made to Heermann and Herzog, "Mikroskopische und mechanisch-technische technische Textiluntersuchungen," Berlin, 1931; J. M. Matthews, "Textile Fibers," New York, 1924; M. A. el Kelaney and G. O. Searle, Proc. Roy. Soc., B. 1930, **106**, 357. The tentative methods for the identification of textile fibres given in A.S.T.M. D276–37T (Proc. Amer. Soc. Testing Materials, 1937, **38**, 1174) are of assistance in the identification of the commoner vegetable fibres.

BAST FIBRES.

Flax.—Flax fibre is obtained from the bast of the stems of the flax plant, *Linum usitatissimum*, Fam. Linaceæ. Linseed oil is derived from the seed of the same plant. The varieties grown for oilseed have, however, different characteristics from the fibre flax plant, they are cultivated chiefly in warmer countries, *e.g.* Argentine, India and North America, and do not yield a valuable fibre. Flax is grown for fibre in temperate countries, notably in Russia the largest producing country, and in the Baltic States, Poland, Belgium, France, Germany, Holland and Northern Ireland. The chief uses of flax are for the manufacture of linens, for making canvases capable of resisting exposure and hard usage, *e.g.* sailcloth, tent-cloth, tarpaulin, etc., and for the production of strong threads and twines. Linen rags and cuttings are a valuable paper-making material imparting strength and "wetness" to pulps in which they are incorporated.

Cultivation and Preparation of the Fibre.—Flax is an annual which reaches a height of about 3 ft. The plant consists of a single slender stem usually devoid of side branches other than those bearing the flowers, which may be either blue or white according to the variety. Recent plant breeding work has now made available new strains, such as the Stormont varieties, and the Liral varieties (the latter having been produced by the Linen Industry Research Association, Lambeg, Northern Ireland) which yield 50% more fibre per acre than the ordinary commercial varieties. The cultivation of flax presents no special difficulties. The seed is sown thickly and can be grown in almost any type of soil that is neither excessively light nor extremely heavy. The crop takes about 14 weeks to mature and, in order to obtain the best fibre, should be harvested before the seed becomes fully ripe. The plants are harvested by pulling, either by hand or by means of mechanical flax pullers. If the seed is to be saved, as is frequently the practice, deseeding or rippling is carried out by drawing the heads of the stems through coarse rippling combs which remove the seed bolls. Mechanical rippers may now be employed.

Retting, the next very important stage in the isolation of the fibre, has for its purpose the loosening of the fibre strands from the central woody core of the stem, so that, in the subsequent processes, the fibre may be separated from the stem with the minimum of breakage, waste and loss of strength. Sub-division of the larger fibre bundles should also follow as a result of successful retting. As seen in a transverse section of the stem, the strands of fibre form a single ring of adjacent, but usually separate, fibre bundles situated in the soft bast tissue which lies immediately under the cortical layer and surrounds the woody core. Ordinary retting processes consist essentially of the fermentation of the pectinous material of the middle lamellæ joining together the thin cell walls of the soft bast. This is effected by micro-organisms, especially *Granulobacter pectinovorum* (= *Amylobacter pectinovorum*), naturally present on the stems. After retting, separation of the fibre strands from the woody core and from each other is easily effected. Several different systems of retting are practised:

Dew Retting.—This process, which is very commonly employed in Russia, and to a certain extent in other countries, consists in spreading out the freshly pulled straw on the grass in meadows and leaving it exposed to the action of the weather until it is sufficiently retted. The straw may be turned from time to time but otherwise receives no attention. Dew retting is the cheapest form of retting and the simplest and easiest to carry out, but dependence on climatic conditions renders the method incapable of control and uncertain in result. Under ideal conditions, however, a first class product can be obtained.

Water Retting.—There are two different methods of water retting, Irish dam retting and Courtrai, or double, retting. The Irish method is carried out by the farmer who has grown the crop. Bundles of the straw are packed in a dam or pond, are sunk by weighting with stones, and are left to steep. From 9 to 10 days' retting is usually required. The Irish method has the disadvantage that every small cultivator produces a slightly different product and the spinner is therefore supplied with a large number of small and varying batches of fibre.

The Courtrai system of double retting in the sluggish River Lys yields the highest qualities of commercial flax. The straw, which is not retted until the summer following that in which it was harvested, is packed into wooden crates which are moored to the river bank and submerged in the water. The crates are lined with sacking to prevent the entry of river mud, etc. The first retting occupies about a week, after which the straw is removed, dried in a field, and then given a second retting of 4 or 5 days. The flax retted in the Lys is grown over a wide area and transported to central retteries on the river for treatment by experienced retters. This system enables a highly uniform product to be obtained and allows of the fibre being graded in bulk. Dam retting is also practised on the Continent.

Tank Retting.—Of the many alternatives proposed to ordinary dew and water retting, warm water tank retting has been the method most generally adopted and tank retteries are now to be found even along the banks of the Lys. The advantages of the method are that it can be carried out all the year round, that it is quicker than ordinary retting, and that it is better capable of control. The straw is packed in large tanks provided with steam coils for heating and is frequently given a few hours' preliminary leaching in water. The water, which dissolves a considerable amount of the water-soluble material from the straw, is either run away or is diluted considerably with fresh water. In this way material which would provide food for non-retting micro-organisms is removed and the development of too great an acidity is avoided; as a consequence the pectic fermentation proceeds smoothly and the danger of the fibre being weakened during drying by the presence of acids is minimised. As an alternative to leaching, a slow flow of water may be allowed to percolate through the vat during the course of the ret. The actual retting takes place at a temperature not exceeding 35–37°C. and usually at a somewhat lower temperature, especially towards the end of the operation. At the conclusion of the ret the straw is well washed, either with cold water or sometimes with a dilute alkaline solution.

Numerous modifications of normal vat retting have been proposed, *e.g.* Carbone's method using *Bacillus felsineus* and Rossi's aerobic ret which requires aeration of the retting liquor. The acceleration of the process by the addition of various chemicals has likewise been the subject of a number of patents. Various efforts have also been made to devise a continuous retting process. Thus in Schneider's channel retting the straw is placed in open crates with perforated sides. These crates, which are submerged in a long channel, move slowly forward against the current of water at such a rate that, by the time they reach the end of the channel, retting is complete. The impossibility of maintaining the cleanliness of the channel has proved a great difficulty. As a means of facilitating the handling of flax during retting processes, a method whereby the straw is sewn into "mats" has recently been devised. Chemical methods of retting have also received attention, *e.g.* Peufaillit's system in which the straw is cooked with water in the presence of a hydrocarbon, the Opitz process, which is worked in Germany, the Tergan method and the Decuypère-Dujardin process. Finally, it is possible to dispense with the retting process and prepare the fibre for spinning by purely mechanical means (crimper-breaker). Coarse convases are now being manufactured from fibre thus prepared. Biological retting, in one form or another, remains, however, the normal method of separating flax from the straw.

For further information concerning the theory and practice of flax retting, the following authors should be consulted: G. Ruschmann, "Grundlagen der Röste," Leipzig, 1923; J. Text. Inst. 1924, **15**, T61; J. W. Porter, Text. Manuf. 1926, **52**, 368; W. H. Gibson, J. Text. Inst. 1936, **27**, P298.

Eyre and Nodder (*ibid.* 1924, **15**, T237) have studied the development of acidity, both total and "permanent" (*i.e.* due to acids other than carbonic) during the course of tank retting under various conditions. They recognise four stages in retting and propose acidity measurements as a means of determining the technical end-point. Similar results were obtained by Porter. The acids produced in biological retting are members of the acetic acid series; lactic acid may also be formed under certain conditions (Störmer, Zentr. Bakt. II 1904, **13**, 309; G. Ruschmann, Mitt. des Forschungs-Inst. Sorau, 1921, **2**, No. 12).

After retting the flax is dried, usually in the open air. Artificial drying, in tunnel driers at 35–40°C., is frequently practised in conjunction with tank retting, but the resulting fibre is considered inferior in quality to that dried naturally. In the next process, known as breaking, the dried straw is passed between a number of pairs of rotating, coarsely fluted rollers which, without damaging the fibre, break the central woody core into short lengths. The flax is then scutched by means of machines provided with wooden blades which strike the broken straw and expel the short pieces of stem. Large capacity turbine scutching machines which completely mechanise the processes of breaking and scutching have been introduced, but do not give such good results as can be obtained by hand with an ordinary scutch wheel. Preliminary scutching with a turbine scutcher, followed by hand treatment with a scutch wheel is, therefore, often practised. The by-products of scutching are the fragments of woody stem, known as shive, and scutching tow. The shive is burned and the scutching tow is utilised in the manufacture of tow yarn.

After scutching the fibre is in the state in which it is sold to the spinner. Its value will depend on the success with which each of the foregoing operations, from the sowing of the seed to the scutching of the straw, has been carried out. No satisfactory, simple scientific test has been devised by means of which spinning quality can be determined. An expert, handling and examining a representative portion of the fibre, can assess its value with a fairly high degree of accuracy. Judgment is based on such properties as suppleness, lustre, "feel," and to a lesser degree colour which, however, varies with the mode of retting.

The conversion of raw fibre into yarn involves the following operations. First, a hand combing known as "roughing" followed by hackling, a machine combing with successively finer combs. In the manufacture of the finest grades of linen the flax is hand-dressed prior to hackling and a more even final product is thereby obtained. In the next process, known as "preparing," the fibre is worked into a rove which is spun either by the wet or by the dry spinning process. Wet spinning, which is essential for the production of fine yarns, is accomplished by passing the rove through a trough of hot water.

Flax is not readily bleached, and long and elaborate methods are necessary to attain the desired result without tendering of the fibre. Bleaching is invariably accomplished either in the yarn or the piece and the processes used are either (*a*) an entirely chemical bleach effected by a series of alkali boils alternating with bleaching with bleaching powder solution and "souring" with acid, or (*b*) in the case of delicate and expensive fabrics, sun bleaching on bleaching greens in conjunction with mild chemical treatment. In the manufacture of sail-cloths, canvases, tarpaulins and similar heavy materials that are subject to hard wear and exposure to the weather and the attack of micro-organisms, the grey yarns are frequently given a boil in dilute alkali. The fibre is thereby cleaned, purified and freed from easily hydrolysable material and the yarn acquires an improved colour, better weaving properties and greater resistance to bacterial action (Elkin, J. Text. Inst. 1935, **26**, P201) (*v.* BLEACHING, Vol. II, p. 11). In the finishing of linen the cloth may either be calendered or it may be subjected to beetling, a pounding of the roll of cloth with wooden hammers. The fabric is thereby closed and the beautiful, characteristic finish produced.

In recent years considerable interest has been shown in the treatment of flax by "cottonisation" processes, especially in central European countries. Cottonisation is merely chemical retting carried to its extreme so that the flax is reduced to its ultimate fibres, in which form it can be mixed with cotton and spun on cotton spinning machinery. The advantages to be gained are the possibility of utilising tow, low grade flaxes and linseed fibre and the elimination of the more expensive flax spinning operations. A great variety of different methods of cottonisation have been proposed, mostly they involve alkaline cooking of one type or another. The desiderata are that the cellulose of the fibre should not be degraded, that the fibre should be properly and evenly separated, and the fibres should not adhere to each other on drying. Cottonisation has reached the stage of commercial production. Reference should be made to G. Kränzlin, Faserforschung, 1921, **1**, 121; K. Schneider, *ibid.* 1937, **12**, 169; F. Tobler, *ibid.* 1937, **12**, 178; W. Bratowski, Textilber. 1937, **18**, 10, 12.

Mention must be made of the possibilities of finding profitable outlets for the straw of flax grown for linseed of which, at present, a considerable tonnage is burned annually. The fibre obtained from linseed straw is too short and coarse to be suitable for flax spinning. Mechanical extraction of fibre suitable for use as an upholstery tow has been practised to a small extent in the United States of America. Other possible methods of utilisation are mechanical separation of the fibre followed by cottonisation or the pulping of the material for conversion into paper. The use of the separated bast fibre for paper pulp manufacture would probably be uneconomic and the pulping of the whole straw presents certain difficulties. Thus for example, owing to the chemical and physical differences between the shive and the bast fibre, all normal digestion processes, when carried far enough to cook the shive properly, are found to over-cook and weaken the bast fibres. The fibres obtained from the shive are, moreover, very much shorter than the bast fibres. The more important contributions to the paper-making value of flax straw are as follows: Kellogg, Shaw and Bicking, Paper Trade J. 1923, **77**, 43; Schafer, Bray and Peterson, Pulp and Paper Mag. Canada, 1927, **25**, i, 209; Bray and Peterson, Paper Trade J. 1928, **86**, No. 3, 48; Schafer and Peterson, *ibid.* 1928, **86**, No. 3, 51; Schafer and Bray, Ind. Eng. Chem. 1929, **21**, 278; J. L. Merrill, U.S. Dept. Agric. Bull. No. 322, 1916; Jayme, Pfretzschner and Ditz, Papier-Fabr. 1938, **36**, 46.

The dimensions of flax ultimate fibres given by Heermann and Herzog are length 10–38 mm., width 14–40μ. It appears, however, that the dimensions of the ultimates vary with their position in the stem (E. Slattery, J. Text. Inst. 1936, **27**, T101). Flax ultimate fibres do not exhibit convolutions as do cotton fibres. They possess narrow lumens and at intervals along their length show node-like swellings and cross-markings. The microscopic characteristics of flax ultimates are very fully described by C. R. Nodder (*ibid.* 1922, **13**, T161). The same author (Trans. Faraday Soc. 1924–25, **20**, 251) gives a valuable review of information concerning the structure, double refraction, pleochroism, X-ray examination, drying twist and swelling phenomena of flax fibre.

Analysis of Irish flax by A. G. Norman (Biochem. J. 1936, **30**, 832) gives, on a moisture-free basis, cellulose (Norman and Jenkins' modification of Cross and Bevan's method) 91·2%, lignin 3·3%, total furfuraldehyde yield 2·3%, cellulose furfuraldehyde yield 1·9%, xylan in cellulose 3·0%, furfuraldehyde from hemicellulose 0·4%.

It was formerly supposed, on insufficient evidence, that pectin was the non-cellulosic constituent of flax which dissolved, and accounted for the loss in weight (up to 25%), which occurs when linen is boiled in alkaline liquors. It has now been established that the pectin content of flax is too low to account for more than a small proportion of the non-cellulosic material in the fibre. It is probable that the pectin in flax free from cortical tissue occurs only in the middle lamellæ separating the ultimate fibres in the fibre bundles. The constitution of flax pectin has been studied by Ehrlich and Schubert (Biochem. Z. 1926, **169**, 13), who prepared their product by boiling flax with water under pressure and obtained a yield of water-soluble material, "Hydratopektin," amounting to 16% of the weight of the dry flax.

Extraction with 70% alcohol separated the "Hydratopektin" into 55% of hexopentosan (galactan-lævulosan-xylan-diaraban) and 45% of the $CaMg$ salt of Pektinsäure (not identical with other workers' pectic acid; Ehrlich's nomenclature is his own). For Pektinsäure, Ehrlich and Schubert suggest the formula, $C_{46}H_{68}O_{40}$, corresponding to diacetyl-arabino-xylo-galacto-dimethoxyl-tetragalacturonic acid. S. T. Henderson (J.C.S. 1928, 2117) used the ammonium oxalate extraction method to isolate the pectin and assigned to flax pectic acid the formula $(C_6H_{10}O_5{\cdot}4C_6H_8O_6-H_2O)_n$ galactose tetragalacturonic acid. This conclusion was criticised by Norris (Biochem. J. 1929, **23**, 195) who supported Nanji, Paton and Ling's well-known galacto-arabino-tetragalacturonic acid ring-formula for pectic acid on the grounds that the yield of furfuraldehyde from flax pectic acid was too high and the uronic acid content too low for agreement with the requirements of Henderson's formula. It has since been pointed out, however, by Norris and Resch (*ibid.* 1935, **29**, 1590), that Nanji, Paton and Ling's formula was based on an incorrect value for the yield of furfuraldehyde obtainable from uronic acids. In view of the incompleteness of our knowledge of the chemistry of the pectins, any attempt to assign a formula to flax pectin must, at present, be received with caution. Neither Henderson nor Norris confirmed the presence of xylose or acetic acid among the hydrolysis products of flax pectin and it seems clear that the material investigated by Ehrlich was not identical with that examined by other workers. The xylose he obtained may have been derived from partially lignified tissue associated with pectins in the cell wall.

The constituents of the cell wall of flax fibre have been investigated by Schmidt, Haag Abele and Sperling (Ber. 1925, **58** [B], 1394), who treated the fibre with ClO_2 and Na_2SO_3 and put forward the hypothesis that the incrustants are esters of a phenolic substance and polysaccharides united by the carboxyl group of galacturonic acid. A. E. Cashmore (J.C.S. 1927, 718) examined mechanically-separated fibre which had been washed free from extraneous matter, extracted with alcohol-benzene, freed from pectins with ammonium oxalate, and from free hemicelluloses with cold 4% $NaOH$. The purified fibre had an α-cellulose content of 82·8% and still contained 15–16% of material soluble in 2% $NaOH$, most of which, since the middle lamellæ constitute only a small percentage of the weight of the fibre, must be present in the cell walls. Hydrolysis with 1% H_2SO_4 at 130–140°C. yielded a mixture of sugars among which glucose, galactose, xylose and fucose were identified. Treatment with water at 140–150°C. produced about 4% of hemicellulose, but there still remained in the fibre about 10% of material soluble in boiling, dilute $NaOH$. Cashmore concluded that the non-cellulosic portion of flax fibre is composed of a hemicellulose, bound to the cellulose either by a glucosidic linkage or by means of the carboxyl of the "-uronic anhydride group" together with more firmly held material of unestablished constitution. Henderson (*l.c.*) isolated 2% of hemicellulose as a $MgCa$ salt and about 5% of a hexopentosan by boiling flax straw with water under pressure.

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Hemp.—Common or true hemp, *Cannabis sativa*, may, like flax, be cultivated either for fibre or oilseed, *v.* HEMPSEED OIL. The plant is grown in Eastern countries as a source of narcotics, *e.g.* hashish, bhang. Confusion has, unfortunately, arisen from the use of the word hemp in the names of other distinct and completely different fibres such as Sunn hemp (*Crotalaria juncea*), Manila hemp (*Musa textilis*) and New Zealand hemp (Phormium). True hemp is strong and durable and more closely resembles flax than any other fibre; indeed, hemp is often used as a substitute for coarse flax. For many centuries it was the chief rope-making fibre but has now to a great extent been displaced by Manila hemp for this purpose. In other fields the position of hemp has declined in favour of jute which, although weaker and less durable, is cheaper and more easily spun. Sunn hemp is also a serious competitor. Hemp is now employed mainly in the manufacture of strong twines and threads, net twines, carpet warp, canvas, sailcloth and ropes of high quality. The tow is used for tarred oakum and for packing pumps, engines, etc. Hemp is also a useful paper-making material, reaching the mill in the form of rags, old ropes and cordage, etc. It is used in good quality wrappings and, by reason of the ease with which it fibrillates, it is specially suitable for thin papers, *e.g.* cigarette tissues and India printings. According to Dewey and Merrill (U.S. Dept. Agric. Bull. 404, 1916), hemp hurds, *i.e.* the fragments of woody stem separated from the bast in scutching, are suitable for the manufacture of printing papers when treated by the soda process. The Pomilio (chlorine–soda) process of pulping is claimed to give good results with hemp straw.

The more important hemp-producing countries are Russia, Italy, Jugoslavia, Rumania, Poland, Hungary and China. The plant, which can be grown on low moorlands too infertile for most other crops, is a diœcious annual with a straight, undivided stem, from 5 to 10 ft. or more in height. The female plant matures later than the male, a fact which has proved a difficulty in the mechanisation of harvesting. The fibre is obtained from the straw by water retting or dew retting in a manner similar to that used in dealing with flax. After retting the fibre is dried and scutched. The separation of the fibre from the straw by mechanical means is being practised (green hemp); hemp lends itself to this process more readily than does flax. Cottonisation has now reached the stage of commercial production. C. Levi (18th International Cotton Congress, 1938, 333) gives staple diagrams of cottonised hemp and discusses the spinning of the material. Cottonised hemp has proved very difficult to spin alone, but it can be mixed with cotton in proportions up to 50% to yield yarns of satisfactory quality.

Hemp ultimate fibres have an average length of about 22 mm. and closely resemble those of flax in their microscopic characteristics. The fibres obtained from the hurds have an average length of about 0·7 mm. compared with an average length of 0·2 mm. for the fibres of flax shive. The following analytical data are due to Schafer and Simmonds (Ind. Eng. Chem. 1929, **21**, 1241):

	Fibre. Dry material.	Hurds. Dry material.	Whole stalk. Dry material.
	%	%	%
Soluble in alcohol–benzene . .	12·0	7·9	9·4
Soluble in hot water . . .	12·0	5·4	10·5
Soluble in 1% NaOH solution	29·5	24·7	29·1
Lignin . . .	7·3	23·3	18·4
Pentosans (total).	6·5	20·5	16·9
Cellulose . . .	61·2	50·5	59·4
Pentosans in cellulose	2·4	11·5	10·0
Ash, total . .	5·3	1·6	3·0
Ash, soluble in hot water . . .	2·3	1·2	1·5

Sunn Hemp.—*Crotalaria juncea* is a leguminous plant grown in many tropical countries as a cover crop or green manure. In India it is cultivated for its fibre, variously known as Sunn hemp, Sann hemp, Indian hemp, or Bombay hemp.

Cultivation and Preparation of the Fibre.—The production of the fibre is a peasant industry and the methods employed differ somewhat in detail in different localities.

The plant is grown in small patches from seed thickly sown so that the stems shall be tall and erect with the minimum of side branching. The crop is harvested after 4 or 5 months either by pulling or by cutting the plants close to the ground. After lying for 2 or 3 days in order that they may shed their leaves, the stems are made up into bundles and retted for 4–7 days. When fully retted they are pounded with stones and the fibre stripped by hand, washed and finally dried in the sun. The fibre produced by the small cultivators is collected at suitable centres and transported to ports of shipment where it is graded and baled.

Description.—The commercial product consists of soft, ribbon-like strands up to about 5 ft. in length and resembling true hemp in appearance. The fibre is liable to be contaminated with dirt and foreign matter—mainly owing to the crude methods of the native producer and the frequent absence of any but muddy water for retting.

Sunn hemp is used as a substitute for true hemp in the manufacture of cordage, tarpaulins, canvas, sacking, etc.

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Jute.—Jute, the cheapest of the textile fibres, is obtained from the stems of two very similar species of Corchorus, viz. *C. capsularis* and *C. olitorius* (Fam. Tiliaceæ). Practically the entire world crop is produced in India, mainly in Bengal where conditions are particularly suitable for its cultivation. Jute is utilised in greater quantities than any other vegetable fibre except cotton. It is used for the manufacture of bale coverings, sacking, bagging, tarpaulins, carpets, rugs and matting; it forms the backing of linoleum and oilcloth; and, in conjunction with other fibres, it enters into the composition of a variety of fabrics. Waste jute is used in the manufacture of brown wrapping papers.

The production of jute is entirely a peasant industry. The plants, which are annuals, take 3 to 4 months to mature. Their slender, cylindrical stems grow to a height of 5–13 ft. and a diameter of ½–1½ in. The crop is generally considered fit for cutting when the flowers begin to fade and the seed pods to set. Earlier cutting is said to yield a weaker fibre and later cutting a coarser, inferior fibre. The fibre is obtained from the bast by retting, preferably in a stream, for a period which may vary from a few days to a month according to the temperature of the water and other factors. When retting has proceeded far enough, the ribbons containing the fibre are stripped from the stems by hand, beaten on the surface of the water, freed from adhering bark, wrung out, and hung on lines to dry in the sun. Finally the fibre is baled. More than half the annual crop is now consumed in Indian mills.

Description and Properties.—Jute is a soft, lustrous fibre varying in colour from pale yellow, or sometimes silvery grey, to brown. The strands are up to 8 ft. or more in length. Jute is much weaker than flax and hemp and is considerably less durable, suffering a gradual deterioration with age, especially in the presence of moisture. Owing to its woody nature, it is necessary when spinning jute to submit the fibre to a preliminary process known as batching in which it is softened by treatment with water emulsions of mineral oil. Jute is readily dyed, usually in the yarn or the piece. Acid, substantive or basic dyes (which may be used without a mordant), and, less frequently, sulphur dyes are all employed. Unless a bright or clear colour is required, the fibre is dyed in its natural state, as it is difficult to bleach jute satisfactorily and the bleached material is liable to discolour on exposure to sunlight. If bleaching is necessary it is effected either by sodium hypochlorite, or by permanganate followed by sodium sulphite, or by both processes successively. Careful control is necessary as the fibre is very susceptible to attack during bleaching.

The ultimate fibres of jute range from about 0·75 to 4 mm. in length and from 10 to 30μ in width. Their lumens show considerable variation in diameter and corresponding fluctuations occur in the thickness of the cell wall. In cross-section the ultimate fibre is a polygon—usually with 5 or 6 sides. An analysis by Lehne and Schepmann (Z. angew. Chem. 1925, **38**, 93) gives, for an average sample of clean jute, moisture 11·42%, ash 0·73%, aqueous extract 3·84%, fats, waxes, etc. 1·03%, cellulose 69·63%, lignin 18·83% and furfuraldehyde yield 11·38%. W. G. MacMillan and M. K. Sen (J. Text. Inst. 1939, **30**, T73) give figures ranging from 0·14 to 0·55% for the natural wax content of jute. A series of samples representing different quality jutes analysed by A. G. Norman (Biochem. J. 1936, **30**, 831), furnished the following results (dry fibre): cellulose 69·8–78·0%, lignin 10·4–13·9%, total furfuraldehyde 9·6–11·2%, xylan in cellulose 10·9–12·8%. The better grade samples tended to have a higher cellulose content, but the difference in composition of the samples was not very marked and was probably partly accounted for by differences in the cleanliness of the fibre.

Jute is a highly lignified fibre and was considered by Cross and Bevan to be composed of lignocellulose—a compound cellulose. Subsequent work, particularly X-ray investigations, has, however, led to the modification of the views of these pioneer workers, and their theory of chemical union between the cellulose and the lignin is no longer accepted. Lignin is now considered to be present as an amorphous, incrusting material. A series of papers dealing with the chemistry of jute lignin has been published by P. B. Sarkar (J. Indian Chem. Soc. 1931–35). Sarkar has found jute lignin to resemble lignins from other sources and he puts forward the view that its constitution is that of a fully saturated compound with a molecular weight of 830 containing in the molecule 5 methoxyl groups in ether linkage, 5 hydroxyl groups and one methylenedioxy group.

Chowdhury and Saha (*ibid.* 1930, **7**, 347), have examined the hemicellulose from jute. They isolated their material by extracting, with 17·5% sodium hydroxide solution, jute which had previously been extracted with chloroform to remove resins, delignified with ClO_2 and successively extracted with benzene, alcohol and boiling water. The yield amounted to 8·6% of material which gave 28·1% of furfural on boiling with 12% HCl. When jute-hemicellulose was hydrolysed with 2·5% H_2SO_4, galactose, lævulose, arabinose, xylose, and uronic acids were identified among the hydrolysis products.

Bibliography.—E. Nonnenmacher, "Die Jute," Berlin, 1930; S. G. Barker, J. Roy. Soc. Arts, 1938, **86**, 457, and J. Text. Inst. 1939, **30**, 273; R. S. Finlow, *ibid.* 1939, **30**, 352; H. L. Parsons, *ibid.* 1939, **30**, 311.

JUTE SUBSTITUTUES.—A number of plants, particularly those belonging to Fam. Malvaceæ and Tiliaceæ, yield bast fibres similar to jute and capable of being spun as a substitute for it or in admixture with it. The more important of these fibres are Ambari and China Jute.

Bimlipatam Jute (Ambari, Mesta or Deccan Hemp), a fibre closely resembling true jute in character, obtained from the stems of *Hibiscus cannabinus*, a plant cultivated in parts of India. The fibre is separated by retting in a manner essentially the same as that employed for jute. The product is rather coarser than true jute but can be used for practically all the same purposes. Other varieties of Hibiscus, *e.g. H. sabdariffa* (Roselle fibre), *H. esculentus*, and *H. lunariifolius*, also yield useful fibres but are of minor importance commercially.

China Jute, *Abutilon Avicennæ*, the Indian mallow, is cultivated in China and the fibre exported under the name of "China jute."

Fibre from plants of the *Sida* spp. and of the *Urena* spp. (especially *Urena lobata*) is also capable of being used as a jute substitute.

The extraction of fibre from *Spartium junceum* (Spanish broom, "Ginesta") has received attention in recent years in Italy. The fibre may be used for the manufacture of ropes, cords, yarns and coarse fabrics. In the cottonised state the fibre may be enployed in the manufacture of finer fabrics. Fibre was extracted from the common nettle in Germany during the war of 1914–18, and more recently experiments have been made with hop fibre.

LEAF FIBRES.

Manila Hemp (Abaca).—Manila hemp is the product of *Musa textilis*, a member of the banana family bearing inedible fruit. Production of the fibre is an almost complete monopoly of the Philippine Islands. A small quantity of Manila is now being exported from Sumatra and from British North Borneo.

Cultivation and Extraction.—The plant requires a good soil, tropical temperature and a wet climate. The fibre occurs in the broad leaf stalks which grow wrapped round the slender central stem in overlapping layers to form a thick pseudo stem, up to 20 ft. in height when fully grown. Mature plants consist of clumps of 20 or more of these upright trunks in different stages of development. The trunks are cut as they mature, an area being cut over at intervals of about 6 months. The best fibre is obtained just before flowering, when the trunk is 2 or 3 years old.

Formerly, the crop was entirely in the hands of small-holders and the cultivation of the plant was carried on under traditional and unscientific lines. An increasing amount of fibre is now coming from scientifically-run plantations in the Davao region. The fibre is, for the most part, still obtained by arduous hand-scraping methods or by means of simple machines, but on a few large estates, decorticating machines such as are used for sisal are being employed. The yield of fibre amounts to 1½–2½% of the weight of the fresh stalks. The final product is graded according to official standards.

Description.—The Manila hemp of commerce is composed of strands up to 15 ft. in length and varying in colour from pale straw to brown. The strands are of more or less circular cross-section and are composed of ultimate fibres from 3 to 12 mm. in length and 16–32μ in width. The ultimate fibres are straight and stiff, have well-defined lumens and in appearance closely resemble those obtained from sisal.

Manila contains about 9% of lignin and 74–77% of cellulose on the moisture-free material; analytical figures vary, however, with the grade of the fibre. The ash content affords a useful indication of the grade of the fibre, the figure showing a more or less progressive increase with the inferiority of the grade of the fibre (Bull. Imp. Inst. 1922, **20**, 101).

Little systematic research has been done on Manila hemp. Dantzer and Roerich (Bull. agence gén. colonies, 1933, **26**, 281), have recorded determinations of certain of the mechanical properties of the fibre. The variability of the tensile strength of the fibres, even when of the same origin in the pseudo stem, has been pointed out by M. Tirona (Philippine J. Sci. 1932, **48**, 243). Manila hemp is naturally slightly acid and the relation between the acidity of the fibre and its tensile strength has been investigated by P. L. and H. E. Sherman (Philippine J. Sci. 1928, **37**, 21), who found a decrease in tensile strength with an increase in acidity. The acidity of Manila may lead to internal corrosion when it is used for the fibre of wire ropes. Methods of estimating the acidity of the fibre are given by J. E. O. Mayne, Safety in Mines Research Board, Paper No. 97, and B.S.I. Specification No. 525, 1934, in which it is specified that the acidity of Manila hemp intended for fibre cores should be such that not more than 2·0 ml. of $N/10$ KOH is required for the neutralisation of 10 g. of fibre when tested by the B.S.I. method. J. E. O. Mayne (*l.c.*) has identified the acids chiefly responsible for the acidity of Manila as acetic and formic acids, present in the quantities of 0·047% formic acid and 0·147% acetic acid.

Uses.—The main use of Manila hemp is for the manufacture of ships' ropes and cables, an important field in which it holds an unrivalled position. The fibre is also used for the manufacture of small ropes, cords, binder twine, etc., but it is losing ground in these markets in favour of sisal. The tow finds a limited application in upholstery. Waste fibre and old ropes are employed for the manufacture of a long-fibred paper pulp from which is made the exceedingly strong Manila paper used for cement sacks, envelopes, etc.

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Phormium Tenax (New Zealand "Hemp."—*Phormium tenax*, New Zealand "hemp," New Zealand "flax," is a member of the Liliaceæ, indigenous to New Zealand, which is the only important producing country. The plant is cultivated to a lesser extent in St. Helena and the Argentine and can be grown for fibre in most temperate countries, including the United Kingdom.

Cultivation and Extraction.—Most of the fibre of commerce is obtained from wild Phormium growing in swamps. Cultivation in plantations, which gives a considerably higher yield and facilitates and cheapens the collection of the leaves, is being encouraged. Research on the breeding of improved strains is in progress (Massey College, New Zealand).

The plant consists of groups of leaves arranged in the form of "fans" springing directly from rhizomes. Cutting of the leaves first occurs when the plant is 5–8 years old. At this age the leaves, which are broad, relatively thin and covered with a hard cuticle, are about 10 ft. in length. The leaf fans are cut off a few inches from the ground, leaving the central bud. A fresh crop of leaves is not ready for harvesting for another 3 or 4 years. The character and structure of the leaves makes efficient separation of the fibre in an unimpaired condition difficult to accomplish. Stripping machines are employed, but those at present available are not considered to be entirely satisfactory. After stripping and washing, the fibre is "paddocked," *i.e.* spread out in drying fields for several days to dry and, to some extent, to bleach. Finally, the fibre is scrutched, baled and graded into one of eight Government grades. Wild Phormium gives a fibre yield amounting to 10–14% of the weight of the leaves.

Description.—Phormium fibre consists of long strands which may be about 10 ft. in length and rather resemble Manila hemp in appearance but is however, softer and weaker. The average length of the ultimate fibres is about 6 mm., the minimum length 2 mm. and the maximum 11 mm.

Uses.—The principal use of Phormium is for the manufacture of twines and cordage. It is particularly suitable for purposes demanding a softer fibre than sisal or manila. Coarse fabrics may also be manufactured from the fibre. The tow finds applications as a stuffing material for mattresses, as a binding material for certain plasters, etc.

The suitability of Phormium for marine cordage has been investigated by the Imperial Institute and the Admiralty (Bull. Imp. Inst. 1931, **29**, 1; 1932, **30**, 119; 1933, **31**, 500). The durability of the fibre to exposure and to sea-water proved satisfactory, but the initial strength of Phormium yarns and ropes was liable to be too low to comply with Government specifications. Further work by the Admiralty on tarred Phormium ropes manufactured according to soft fibre specifications gave promising results. Such ropes, when made from a suitable grade of Phormium, were considered to be as satisfactory as similar cordage made from Italian hemp.

Investigation of the paper-making properties of Phormium (M. B. Shaw, G. B. Bicking and M. J. O'Leary, Bur. Stand. J. Res. 1931, **6**, 411) shows that up to 60% of a good quality pulp can be obtained from the fibre. Alkaline cooking of the leaves give a yield of pulp amounting to about 14% of the weight of the fresh leaves which contain approximately 70% of moisture (New Zealand Dept. Sci. Ind. Res., 8th Annual Rept., 1934, 17).

Bibliography.—E. H. Atkinson, Phormium Tenax, The New Zealand Fibre Industry, New Zealand J. Agric. 1921, **22**, 81–86, 203–216, 283–289, 347–356; **23**, 103–107, 298–302; also available as New Zealand Dept. of Agric. Bull. No. 95 (New Series), 1922; E. Goulding, "Cotton and other Vegetable Fibres," London, 1919.

Sisal and Henequen.—Sisal fibre is derived from the leaves of plants of the Agave family (Fam. Amaryllidaceæ), in which it occurs either as serving a purely mechanical function or associated with the vascular bundles. The fibre strands run longitudinally through the leaf and vary in length from a few inches to the full leaf length. A leaf of *A. sisalana* contains approximately 1,000 fibre bundles. The morphology of Agave fibres and their distribution in the leaf is described by F. J. Nutman (Empire J. Exp. Agric. 1937, **5**, 75).

The Agaves are indigenous to South and Central America but have been successfully introduced into most tropical countries. The chief sources of commercial supply are Mexico, Tanganyika, Kenya and the Dutch East Indies.

Mexican sisal or "henequen" is obtained mainly from *Agave fourcroydes*, but other varieties of Agave occur in the Mexican plantations—a fact which is held partly to account for the variability of the Mexican fibre. East African and Dutch East Indian sisal are derived solely from the leaves of *Agave sisalana*. Blue sisal, *Agave amaniensis*, a new species discovered at the East African Agricultural Research Station, Amani, has, however, attracted attention by growing more quickly and yielding a longer and finer fibre than sisalana. Commercial production of this fibre in East Africa may be expected.

Cultivation.—The Agaves are very hardy, little subject to disease, and capable of being grown on soils unsuitable for most other crops. In East Africa *A. sisalana* takes about 3 years to reach maturity by which time its thick, fleshy, tapering leaves have reached a length of 3–6 ft. After a period of leaf production, which varies according to soil and climatic conditions, the plant sends up a tall flowering stem or "pole," which blossoms and soon afterwards withers and dies. Viable seed is rarely produced and propagation is entirely vegetative, being effected either by means of suckers or by "bulbils," small plants which are produced in large numbers in the axils of the bracts on the flower stems.

As cultivated in East Africa and the Dutch East Indies, sisal is essentially a crop for very large, highly mechanised plantations. The leaves are first cut when the plant reaches maturity, *i.e.* when, in East Africa, it is 3 or 4 years old, and subsequently biennially. During its lifetime a plant may be expected to produce 250–300 leaves yielding 3–4% by weight of fibre. Cutting of the leaves is continuous throughout the year.

As they are cut, the leaves are transported on a light railway to a centrally situated factory where decorticating machines mechanically extract the fibre from the pulpy leaf tissue. A current of water passing through the machine simultaneously washes the separated fibre and sweeps away as flume waste the leaf tissue and the fibre too short to be retained in the machine. Thorough washing is necessary in order to preserve the colour of the product. The hanks of fibre are dried either by hanging in the sun or by means of an articial dryer, the latter method being usual in the Dutch East Indies for climatic reasons. The dried fibre passes to brushing machines in which adhering leaf tissue is removed and the fibre combed, straightened and generally improved in appearance. Finally the sisal is baled under high pressure.

The cultivation and extraction of henequen fibre follow similar lines to those described above. Less attention is paid to detail, however, and the fibre is, in general, rather more variable and inferior. The plant differs from sisal in having a considerably longer life but its annual leaf production is lower. For details of the Mexican industry reference should be made to H. T. Edwards (U.S. Dept. Agric. Bull. No. 1278, 1924), and to V. A. Reko (Faserforschung, 1931, **9**, 118).

The profitable utilisation of the various waste products of the sisal industry has been the subject of several investigations.

Decortication Waste.—Of every 100 tons of leaves conveyed to the factory about 3 tons is fibre and 97 tons is waste. This waste material is usually a source of embarrassment. On account of its high acidity and its sugar content, it cannot be returned direct to the land. Most frequently it is either dumped in a ravine or run into a stream which is thereby seriously polluted. On some estates it is burned in the factory furnaces. The calorific value of the waste and various methods of burning it are noted by F. W. Freise (Tropenpflanzer, 1934, **37**, 419). On incineration it will give 11–13% of ash which may be used as a fertiliser. Composting experiments have also given promising results. S. C. Layzell (East African Agric. J. 1937, **3**, 26) describes a scheme whereby a grid at the end of the factory flume retains the solid matter, which is converted into humus by composting, whilst the liquid waste is led away and used for irrigating food crops. The decorticating machines fail to retain about 20% of the fibre in the leaf and recovery of this, mainly short, fibre, in the form of flume tow, may be practised. Flume tow recovery in conjunction with composting would have the advantage of removing from the material which goes to the composting beds that portion of it most resistant to decay.

Paper-making trials on the dried waste (Bull. Imp. Inst. 1930, **28**, 422) show that a good yield of strong, long-fibred pulp can be obtained from it by a mild soda digestion. Pre-treatment of the material to remove as much as possible of the non-fibrous tissue is necessary. Attention has also been directed to the possibility of producing alcohol, either from the sugars contained in the juice of the leaves, or by the hydrolysis and subsequent fermentation of the cellulosic constituents of the solids in the waste. The sugar content (1–4·75%) of East African sisal leaves is too low for commercial utilisation.

Mexican henequen, however, contains considerably more sugar, and sisal grown in other areas may have a higher sugar content than the East African plant. Large scale production of alcohol from sisal leaf juice has been attempted in the French Sudan. Experiments on the production of alcohol from the waste solids are reported in the D.S.I.R., Fourth Memorandum, Fuel for Motor Transport, " Power Alcohol from Grasses, Straw and Waste Vegetable Materials," 1927. It was established that alcohol could be produced without undue difficulty, but the prospects of economic success were not such as to warrant commercial development.

Sisal Boles and Poles.—These materials have no commercial applications. Their suitability for paper-making has been investigated (*ibid.* 1929, **27**, 3). The boles proved to be of little value, but the poles were found to give a pulp capable of commercial utilisation. The limited supply and the cost of collection have, however, precluded their use for this purpose.

Sisal Tow.—The tow produced in the brushing of the fibre is extensively used as a stuffing material for mattresses, etc., and to a less extent for spinning into yarn.

Description and Properties.—Sisal consists of strands of clean, attractive-looking fibre, varying in colour from yellowish to almost pure white in the best grades, and possessing the coarseness and stiffness associated with hard fibres. The strands are horse-shoe shaped in cross-section and are built up of ultimate fibres of 2–5 mm. in length and 7–47μ in thickness. These ultimates are straight and stiff, possess pointed ends, exhibit a well-defined lumen, and in section are polygonal with a polygonal lumen.

The strands of sisal fibre vary in length from those extending the full length of the leaf down to those of the minimum length which will pass the decorticator. Thus even the highest grades contain a considerable proportion of short fibre. F. J. Nutman (Empire J. Expt. Agric. 1937, **5**, 75) found that, for the decorticated fibre, the length-distribution was governed by the formula

$$\log x = 3{\cdot}012\frac{g}{L} - 1{\cdot}012$$

where L is the leaf length and x the percentage by weight of fibre below a length g. In grading the fibre, Nutman considered that the hank obtained from the individual leaf should be taken as the grading unit. Classification can be made by sorting the leaves either before, or during, their passage to the machine. The product will not, of course, be of uniform fibre-length but its length-composition will be known by calculation from the above equation.

Analysis and Testing.—Sisal is a lignified fibre. An analysis of African sisal by Norman (Biochem. J. 1936, **30**, 83) gives cellulose 74·95% (containing 18·56% xylan) and lignin 6·04% on the dry material. A series of analyses on samples from different countries of origin are recorded in the Imp. Inst. Bull. 1915, **13**, 20; 1929, **27**, 441. The figures given for East African sisal are: moisture 7·4–10·2%; water washing loss 0·2–2·8%; α-hydrolysis loss 9·5–11·6%; β-hydrolysis loss 11·2–14·4%; cellulose (Cross and Bevan) 76·3–81·4%; ash 0·5–1·3%.

As a means of assessing fibre-quality chemical analysis is not, however, very informative, there being but little variation in the figures obtained for normally prepared samples, and such differences as are detectable being difficult of interpretation. Measurement of the mechanical properties offers a method of testing more directly related to the uses of the fibre. Thorough sampling is necessary for such tests and the position from which the test samples are selected needs standardisation as the fibre varies, not only from strand to strand, but also along the length of individual strands. The subject has been studied by Nutman (Empire J. Exp. Agric. 1937, **5**, 93) who takes, as most suitable for testing, that portion of the fibre between 20 and 30 cm. from the butt end of the hank. Using special randomization and sampling technique Nutman found, for samples of commercial East African sisal, a tensile strength of 1,100–2,000 g. and a fineness (mg. per 10 cm. length of fibre) of 2·8–4·7. The results were treated statistically and between 600 and 1,000 tensile strength determinations were made on each sample. Temperature and humidity conditions were not stated.

Uses.—The principal use of both sisal and henequen is in the manufacture of binder twine. The fibre is also made into ropes and twines and woven into coarse fabrics. Applications in other fields are extending with increase in knowledge of the properties and potentialities of the fibre.

The possibility of using sisal for marine cordage has been investigated by the Imperial Institute and the Admiralty (Bull. Imp. Inst. 1927, **25**, 359; 1931, **29**, 1; 1932, **30**, 119; 1933, **31**, 30; 1935, **33**, 4). Long period exposure tests with 1½ in. and 3 in. ropes showed that the durability of sisal compared well with that of Manila hemp. It was further found that sisal can be tarred, whereas Manila does not absorb tar readily, and tarred sisal ropes were shown to be capable of replacing those of European tarred hemp. The behaviour of sisal ropes in actual service confirmed these conclusions and led to the partial adoption by the Admiralty of sisal for marine cordage. More recently the War Office has also authorised the use of sisal ropes for many purposes.

Bibliography.—R. Tobler, " Sisal und andere Agavefasern," Berlin, 1931; S. G. Barker, Sisal, E.M.B. Publication No. 64, 1933; Hemp Fibres, Imperial Economic Committee, 24th Rept., 1932, and papers cited above.

Agave Cantala (Maguey).—This variety of agave, although relatively of much less commercial importance than sisal and henequen, yields a valuable, strong and supple fibre. It is grown as a peasant crop in the Philippines, where it is known as " maguey " fibre (*v.* H. T. Edwards, U.S. Dept. Agric. Farmers' Bull. No. 13, 1906) and to some extent on estates in the Dutch East Indies.

Cantala differs from sisal in that the fibre strands are finer and of round, rather than horse-shoe shaped, cross-section. The ultimate fibres, moreover, have thicker cell walls and narrower lumens than sisal ultimates.

For two samples of Java cantala, Nutman

(Empire J. Expt. Agric. 1937, **5**, 100) found an average tensile strength of 791 and 854 g. and an average fineness (in mg. per 10 cm. length) of 2·29 and 2·16 respectively.

Mauritius Hemp.—Mauritius hemp is a leaf fibre derived from *Furcraea gigantea* (Fam. Amaryllidaceæ), a plant which resembles the agaves in its growth and habits. The plant can be grown in most tropical countries but the fibre is produced in commercial quantity chiefly in Mauritius. The tonnage exported fluctuates, increasing with a rise in hard fibre prices, but is seldom very large.

The fibre is obtained both from wild and from plantation.grown plants. It is extracted from the leaves mechanically in small machines, steeped for 36–48 hours in water containing ½% of soap, thoroughly washed, sun dried, brushed and baled. The yield amounts to about 2% of the weight of the leaves.

In general properties Mauritius hemp resembles sisal but it is usually longer, finer, softer and weaker. Locally it is manufactured into twine, coarse cloth and bags for the shipment of sugar. The exported fibre is used for cordage and for binder twine and sometimes for admixture with other hard fibres for rope manufacture.

Piassava.—Piassava is a long, stiff, wiry fibre obtained from the leaf stalks of certain palms. Bahia piassava (*Attalea funifera*) and Para piassava (*Leopoldinia piassava*) exported from Brazil, West African piassava derived from *Raphia* spp., and Madagascar piassava from *Dictyosperma fibrosum* constitute the chief commercial varieties. The fibre is obtained by a prolonged retting of the stalks, and the value of the product depends on such qualities as its stiffness and colour. Piassava is used for making brooms and brushes of various kinds and for the manufacture of baskets.

Raffia.—Raffia (gardeners' bass) is obtained chiefly from Madagascar and consists of thin, flat, fibrous strips derived from the surface layer of the leaflets of certain palms (*Raphia* spp.). The best quality raffia is four or more feet in length and very pale in colour. It is used in horticulture, for hat-making, and in numerous handicrafts.

MINOR LEAF FIBRES.—Among leaf fibres of minor commercial importance may be mentioned: **Mexican fibre** (*Agave heteracantha*), a wiry fibre used as a substitute for animal bristles in the manufacture of cheap brushes; "**bowstring hemps**" (*Sansevieria* spp.), used to a limited extent for cordage and upholstery; **kitul** (*Caryota urens*), employed in the manufacture of brushes and, in upholstery, as a substitute for horsehair; **palmyra fibre** (*Borassus flabellifer*), also mainly used for brush-making; and **crin végétal**, obtained from a palm, *Chamaerops humilis*, and used as a substitute for horsehair.

Bromeliaceous fibres, *e.g.* **pita** (*Bromelia magdalenæ*), **caroa** (*Neoglaziovia variegata*) and **pineapple fibre** are a group of potentially valuable fibres, the exploitation of which awaits the invention of a suitable decortication machine.

Bibliography.—J. M. Matthews, "The Textile Fibers," New York, 1924; C. R. Dodge, "Useful Fiber Plants of the World," Washington, 1897.

FIBRES FROM SEEDS AND FRUITS.

Coir (Vol. III, 258*a*).

Cotton (this Vol. 135).

Kapok.—Kapok is a floss attached to the inner wall of the fruit capsule of *Ceiba pentandra* (=*Eriodendron anfractuosum*), a tall, gaunt tree grown chiefly in Java and less extensively in the Philippines, India, Ceylon and Malaya.

Cultivation and Preparation.—The trees are seldom systematically cultivated and in Java they are mostly grown along the sides of roads and between fields. The trees come into bearing when they are 3 or 4 years old and continue to yield fibre for many years. The pods are either gathered from the tree as they ripen or are collected after they have fallen to the ground. Roughly 100 pods are required to produce 1 lb. of floss, and a mature tree may be expected to yield from about 350 to 600 pods annually. After the pods have been further ripened and dried by exposure to the sun, the husks, etc., are removed by hand, leaving the floss and the small, round, black seeds that are embedded in it. Since these small seeds are not attached to the floss but merely distributed among it, their removal is easily effected, either by the use of small "ginning" machines or simply by spreading the material on a table of wire netting and beating it with bamboo canes until the seeds fall through the meshes.

Description and Properties.—Kapok is composed of fine, silky, highly lustrous, unicellular fibres varying from 10 to 40 mm. in length and 20 to 30μ in diameter. The fibres, which taper to a point at their free end, are smooth-surfaced, circular in cross-section, possess a wide lumen and an extremely thin cell wall approximately 1–1·5μ in thickness.

Chemically, kapok differs from cotton, to which it is botanically related, in containing a much lower percentage of cellulose, 57–67% on the dry material, and a high percentage of pentosans. A number of samples examined by J. J. Hansma (Chem. Weekblad. 1936, **33**, 620), gave values of from 23·5 to 29·0% for the pentosan content of genuine kapok. A pentosan figure falling within this range is not by itself a sufficient proof of the purity of a sample. The commonest adulterants of kapok are cotton waste, which has a very low pentosan content, and akund, which contains up to 35% or more, and it is evident that a sophisticated sample containing both these adulterants might give an apparently normal pentosan value. The adulteration of the material can, however, be detected by a buoyancy determination for which Hansma describes an apparatus. Pure kapok shows only a small diminution in buoyancy after 24 hours; spurious or adulterated samples are revealed by a low initial buoyancy and a marked drop in 24 hours. This test is also of value in distinguishing between new and second-hand kapok. According to Moskowitz, Landes and Himmelfarb (Amer. Dyestuff Rep. 1936, **25**, 220), unused kapok has an ammonia content of less than 0·030% and a urea content of less than 0·015%, and figures in excess of these quantities are definite evidence of the sample being second-hand. A microscopic method of distinguishing between kapok and akund fibres is described by N. J. M. Vorstman (Chem. Weekblad, 1936, **33**, 746, noted in the Analyst, 1936, **62**, 224).

Uses.—Kapok, on account of its resilience, lightness and voluminous nature, is much used for stuffing cushions, pillows, mattresses, etc. Its buoyancy, which is many times that of cork, and its resistance to waterlogging render it specially suitable for use in the manufacture of life-belts and life-jackets. Kapok is also used to some extent as a thermal insulating material. The fibres are structurally unsuitable for spinning.

Kapok Seed Oil.—The seeds obtained on "ginning" kapok constitute a valuable by-product. They contain from 18 to 25% of a light yellow oil resembling cotton-seed oil in its composition and giving a positive Halphen reaction. The higher grades of the oil are used for edible purposes and the lower grades for soap making, etc. The constants for Java kapok seed oil, examined by Griffing and Alsberg (Ind. Eng. Chem. 1931, **23**, 908), were as follows: specific gravity at 25°C. 0·9225; refractive index 1·4691/25°; saponification value 191·6; iodine no. (Hanus) 94·1; acid value 9·65; saturated acids 17·15%; unsaturated acids 76·32%. According to Jameson and McKinney (Oil and Soap, 1936, **13**, 233) the oil expressed from Java kapok seeds contains 45·2% oleic, 32·9% linoleic, 10·2% palmitic, 8·4% stearic, 1·2% arachidic and 0·04% lignoceric acids expressed as glycerides. Similar results were obtained by Crux and West (Philippine J. Sci. 1931, **46**, for the composition of Philippine kapok seed oil.

Very little or no gossypol is present in the oil cake (Griffing and Alsberg) which contains from 4 to 5% of nitrogen and is of use as a cattle feed.

Bibliography.—D. H. Grist, Kapok, Malay. Agric. J. 1923, **11**, 3–27; Kapok, Bull. Imp. Inst. 1926, **24**, 18–36; M. M. Saleeby, The Kapok Industry, Philippine Bur. Agric., Bull. No. 26 (revised ed.), 1922.

"Akund."—"Akund" is the name given to the floss surrounding the seeds of *Calotropis* spp. The floss, which resembles kapok in appearance, is exported from India to a limited extent. It is used in upholstery either alone or in admixture with cotton waste but, being inferior to kapok in resiliency, it is in less demand and realises a lower price. Its quality depends on its colour, cleanness and freedom from seeds and extraneous matter.

Simul or "Indian Kapok."—Simul or "Indian kapok," also produced in India, is the floss of *Bombax malabaricum*. As a stuffing material it is inferior to kapok. Its buoyancy has been shown to compare favourably with that of Java kapok (Bull. Imp. Inst. 1919, **17**, 14). Indian kapok is, however, liable to be contaminated with akund floss which easily becomes waterlogged.

A description of the microscopic characteristics of a large number of different flosses is given by H. Neubert (Faserforschung, 1933, **4**, 227).

E. L. H.

FIBRIN *v.* Blood (Vol. II, 22*c*, 24*a*).

FIBRINOGEN *v.* Blood (Vol. II, 22*c*).

FIBROLITE. A synonym for sillimanite the aluminium silicate Al_2SiO_5 or $Al_2O_3{\cdot}SiO_2$, which is the only known anhydrous natural compound of silica and alumina.

"FIBROLYSIN." A solution of thiosinamine and sodium salicylate (Merck, Darnstadt; Napp, London).

FICHTELITE. A hydrocarbon, found as white or yellowish platy crystals and crystalline crusts in the crevices of lignified pine wood in peat-bogs (Bromeis, Ann. Pharm. 1841, **37**, 304). The monoclinic crystals, both natural crystals and those obtained by recrystallising the material from alcohol or benzene, are interesting on account of their hemimorphic development, there being, as in crystals of cane-sugar and tartaric acid, no plane of symmetry. Localities where fichtelite has been found are Redwitz and several other places in the Fichtel Mountains in northern Bavaria, Kolbermoor near Rosenheim in southern Bavaria, Borkovic and other places in Bohemia, Handforth in Cheshire, Shielding in Ross-shire, etc. For a review of the literature, *see* A. Schmidt, Centr. Min. 1901, 519; F. Plzák and V. Rosický, Z. Kryst. Min. 1908, **44**, 332; A. Rosati, *ibid.* 1912, **50**, 126.

L. J. S.

FICHTELITE, $C_{19}H_{34}$ (Ruzicka); $C_{18}H_{32}$ (Bamberger), m.p. 46°; b.p. 355·2°/719 mm.; *v.d.* 8·66, calc. 8·58 (Bamberger and Strasser, Ber. 1889, **22**, 3361), $[\alpha]_D^{20}$ +19°0 in $CHCl_3$ (Walden, Chem.-Ztg. 1906, **30**, 393), sparingly soluble in cold alcohol, readily in boiling light petroleum which is used to extract fichtelite from decayed wood. It is a stable compound, and may be distilled unchanged over red-hot PbO (Bamberger, Ber. 1889, **22**, 635), it is scarcely affected by boiling with sulphuric acid and bichromate or with 10% $KMnO_4$ solution; cold fuming nitric or sulphuric acid are without action, it is however oxidised to acid products by CrO_3 in acetic (Hell, *ibid.* 498). Equal molecules of fichtelite and iodine at 150–200° yield dehydrofichtelite ($C_{18}H_{30}$ according to Bamberger and Strasser, *l.c.*), a blue-violet fluorescent liquid, b.p .224–225°/38 mm. Bamberger assumed that fichtelite was completely hydrogenated retene, but the relationship of fichtelite (I), retene (II) and abietic acid (III) was first discovered by Ruzicka. Fichtelite heated with 7 atoms of sulphur to 180–250° for 20 hours yielded only 13% retene (R. *et al.*, Helv. Chim. Acta, 1923, **6**, 692). Later Ruzicka and Waldmann (*ibid.* 1933, **16**, 842) heated abietic acid with palladium-charcoal to 300–330° and obtained retene in 90% crude yield:

$$C_{20}H_{30}O_2 \rightarrow C_{18}H_{18}+CH_4+CO_2+4H_2$$

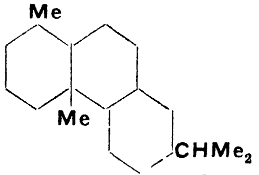
The formation of methane indicating the loss of one CH_3 group is significant, for the authors (*ibid.* 1935, **18**, 611) found that fichtelite heated with the same reagent to 330–370° also lost one CH_3 group as CH_4, as well as 6 mol. H_2, and yielded retene in 85% crude yield. They argue that fichtelite must now be written $C_{19}H_{34}$ and that the equation is

$$C_{19}H_{34} \rightarrow C_{18}H_{18}+CH_4+6H_2,$$

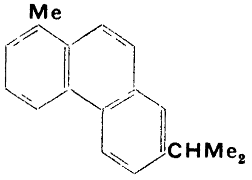
for if fichtelite were perhydroretene the decomposition would have proceeded thus:

$$C_{18}H_{32} \text{ (fichtelite)} \rightarrow C_{18}H_{18}+7H_2.$$

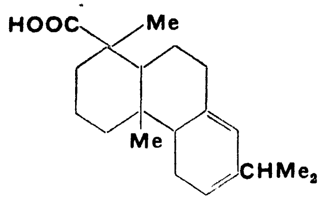
They conclude that fichtelite has almost certainly the formula $C_{19}H_{34}$ and the structure of a dimethyl*iso*propylperhydrophenanthrene in which the only uncertainty is the position of the **Me** group split off on dehydrogenation. Crowfoot's (J.C.S. 1938, 1241) molecular weight determination of fichtelite by X-ray analysis and density determination supports the formula $C_{19}H_{34}$, although other observations in the same paper do not discriminate between the two formulæ.



I.



II.



III.

J. N. G.

FICOCERYLIC ACID, the name given to the acid obtained on saponifying the wax (Gondang wax) from the leaves of the wild fig-tree by Greshoff and Sack (Rec. trav. Chim. 1901, [ii], **20**, 68) was shown to be impure palmitic acid by Ultée (Pharm. Weekblad. 1915, **52**, 1097.

"**FICUSIN**" *v.* FIG.

FIG. *Ficus carica* L. Fig trees grow wild in Mediterranean districts and the fruit is an important article of diet. The fig is cultivated in India, China and California. Many varieties differing in colour and size of fruit are known. The fruit is eaten fresh, dried or preserved. The pulp forms 50% of the weight of the whole fruit and contains large numbers of small hard seeds constituting up to 10% of the weight of the fruit. Certain varieties produce sterile flowers but develop well-formed seedless fruit.

Typical analyses given in percentages are:

	I			II.			III		IV.	
	Whole fruit.	Edible portion	Dried	Pulp and seeds.	Skin	Whole dried.	Pulp.	Seeds.	Whole.	Peeled
Total solids . . .	20·1	15·0	81·2	20·0	14·0	43·0	10·7	94·0	14·3	14·6
Protein	1·34	1·40	4·3	0·7	—	4·1	0·5	—	0·7	0·6
Fat	—	0·3	0·3	0·3	0·1	2·2	—	5·8	0·2	0·3
N-free extract . .	–	11·64	74·2[1]	17·0	8·14	26·2	—	28·1	12·1	12·5
Acid (as citric) . .	0·17	0·21	0·57	—	—	—	0·23[2]	—	0·15	0·17
Sugar	15·5	10·8	—	16·2	5·4	26·1	9·0	—	—	—
Fibre	—	1·17	—	1·3	5·8	8·0	—	55·6	0·9	0·9
Ash	0·58	0·49	2·4	0·7	—	2·5	0·41	1·71	0·4	0·3

[1] Includes fibre.
[2] Acid as malic.

I. American types (Colby, Rep. Agric. Exp Sta. California, 1892–4).
II Italian grown (Paladino, Biochem. Z. 1910, **24**, 263).
III. Egyptian varieties, Azadian (Ann. Falsif. 1927, **20**, 464).
IV. Miller *et al.* (Hawaii Agric. Exp. Sta. Bull. 1937, No. 77, 90)

According to Traube and Fraps (Proc. Amer. Soc. Hort. Sci. 1928, 306) magnolia figs contain total solids 16·8, protein 0·7, sugar 11·8, fibre 1·0 and ash 0·4%. When dried and sulphured this variety is reported as containing 58% sugars (as invert), 0·9% of citric acid and 110 p.p.m. of SO_2 (Read, Texas Agric. Exp. Sta. 47th Ann. Rept. 1934, 159).

Fig syrups are prepared by extraction with water and concentration of the extract *in vacuo* until the sugar content reaches approximately 63%. In Algeria the extracts are allowed to ferment and the resulting wine is used to adulterate grape wines. Fig wine contains mannitol (6–8 g. per litre), the determination of which affords evidence of adulteration. On evaporation of fig wine the mannitol separates together with small amounts of sugar and organic acids.

The principal acids of the fig are citric and acetic. Hotter (Z. Nahrungsm.-Unters. Hyg. 1895, **9**, 1) records 0·0015% of boric acid in the fruit and Arbenz (Mitt. Lebensm. Hyg. 1917, **8**, 98) finds 0·12% of oxalic acid in dried figs.

The dried seeds of fig contain up to 30% of oil which shows the following characteristics: n_D^{25} 1·4775, iodine value 169·4, thiocyanate value 108·4, saponification value 190·1, acid value 0·87, acetyl value 6·1 (Jamieson and

McKinney, Oil and Soap, 1935, **12**, 88). Azadian (*l.c.*) gives rather different data for Egyptian seed oil, viz. d^{15} 0·9253–0·9493, n_{D}^{40} 1·4670–1·4725, iodine value 102·8–117·4, saponification value 193–205. Jameson and McKinney record the oil to contain 1·07% of unsaponifiable matter, and of the total fatty acids 85% are unsaturated. The percentage of fatty acids in glycerides is given as:

Oleic	19·8
Linoleic	35·1
Linolenic	34·2
Palmitic	5·5
Stearic	2·3
Arachidic	1·1

Winton quotes the mineral matter of the fig (as percentage of the fresh fruit) to be

K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3.
0·54	0·01	0·08	0·05	0·01
Mn_2O_3.	P_2O_5.	SO_3.	SiO_2.	Cl.
0·002	0·10	0·04	0·04	0·02

Dried figs also contain Fe 30–40, Cu 3·5 and Zn 1·2–3·6 mg. per kg.

From fig leaves K. Okahara *et al.* (Bull. Chem. Soc. Japan, 1936, **11**, 389; Ber. 1937, **70** [B], 73) isolated "ficusin," *psoralene* $C_{11}H_6O_3$, and also bergapten (*q.v.*).

Branches of trees of the genus *Ficus* (notably *F. elastica*) on tapping yield a milky juice containing a considerable proportion of rubber.

A. G. Po.

FIG WAX. *Cera fica, Gondang, Kondang, Getah, Java* or *Sumatra wax.* A wax consisting largely of esters of lupeol and β-amyrin (Ultrée, Pharm. Weekblad. 1915, **52**, 1097); obtained from the leaves of *Ficus ceriflua* Jungh., in the form of hard brown cakes, m.p. *c.* 60°, d^{15} 1·015 (Greshoff and Sack, Rec. trav. chim. 1901, [ii] **20**, 65).

FILAMENTS, TUNGSTEN. INTRODUCTION.—No account of the manufacture of lamp filaments can be clearly understood unless it is seen against the background of the fundamentals governing the design of the lamp. These latter eventually dictated the present choice of tungsten as a material, and its use in the form of a helix running in an inert atmosphere and later as a double helix or coiled coil.

The advantages of tungsten as a material arise from considerations of the behaviour of temperature emitters, which may be summarised as follows:

When a solid body is heated, it radiates energy over a continuous band of wave-lengths, and as the temperature rises the proportion of energy in the shorter wave-lengths increases. The only part of the energy which is of use to the eye lies between, roughly, 4,000 (violet) and 7,000 (red) A. The proportion of the energy radiated at any temperature in any particular part of the spectrum is determined by the nature of the body and its temperature. The *total* radiation, at a given temperature, is highest for a "black body," to which carbon is the nearest approach, but certain substances may give in one part of the spectrum a higher radiation than a "black body" at the same temperature.

The first desiderata in selecting a material for lamp filaments are therefore that it shall be capable of withstanding as high a temperature as possible, and that it shall have good emitting properties in the visible part of the spectrum. Tungsten is well suited to the purpose particularly because of its very high melting point.

The following figures illustrate the importance of temperature. If power could be completely transformed into light corresponding with average sunlight, the efficiency would be 200 lumens per watt, or if it were all radiated at 5,550A (the greenish-yellow part of the spectrum to which the eye is most sensitive) the theoretical efficiency would be 670 lumens per watt.[1]

Tungsten at its m.p. (3,655°K.) has a theoretical efficiency of 53 lumens per watt, and under practical conditions the highest efficiencies attained are of the order of 20 lumens per watt. Carbon, having a higher m.p. (3,765°K.), would appear to have advantages, but its rate of evaporation at high temperatures is greater than that of tungsten, and in practice it cannot be used except at greatly below the same efficiency.

The only other materials which have been seriously considered as rivals to tungsten are certain carbides, but there are so far no signs that they are likely to be of practical use, owing to their dissociation at high temperatures.

EVOLUTION OF THE FILAMENT LAMP.—The first electric filament lamp was made by Davy in 1802, and his filament was a strip of platinum (m.p. 2,045°K.) heated by means of a battery. A number of improvements of experimental interest followed, but it was not until 1879 that the work of Swan and Edison led to the introduction of a practical lamp, in which a carbon filament was used. The earlier carbon filaments were made by carbonising strips of bamboo, paper and similar materials; later, methods depending on the extrusion of cellulose gels were developed, some of which are in use at the present day. The carbon lamp remained without a rival until 1902, when the metal filaments were introduced. The first of these was osmium (m.p. 2,975°K.), followed in 1905 by tantalum. The tungsten lamp reached the commercial stage in 1906. All of these metal filaments were made by the squirting process; the metal, in the form of a fine powder, was mixed with a carbonaceous binder such as nitrocellulose, starch, dextrin or tragacanth to form a paste which was squirted into threads through sapphire or diamond dies. The organic matter was subsequently burnt off in a diluted hydrogen atmosphere, leaving a coherent thread of sintered metal.

DRAWN TUNGSTEN WIRE.—The next big advance was the production of drawn tungsten wire by Coolidge, in 1909, B.P. 23499/09, and this introduced a completely new technique in metallurgy. Mainly because of the high melting point of tungsten, it was not practicable to produce a wire by the usual processes starting with a cast ingot. Coolidge therefore pressed tungsten powder into a coherent bar which could be first hardened by moderate heating, and then sintered at a high temperature to a compact crystalline bar which was first worked by hot hammering (or swaging) and then at a later stage drawn through dies into a flexible wire. This is in essence the process used at the present day, and it will be described later in detail. The next step in the evolution of the filament is bound up with the invention of the gas-filled lamp. This latter demands detailed treatment, since the whole course of tungsten filament metallurgy has been determined by its requirements, but it is first of all necessary to consider in some detail the basis of filament lamp design.

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[1] Lamp efficiencies are nowadays always given in lumens per watt. The "lumen" is the light radiated through unit solid angle by a uniform spherical source of 1 candle; for practical purposes, a lumen may be thought of as $\frac{1}{12\cdot7}$ of the total integrated light from a source which averages 1 candle in every direction.

Principles of Filament Lamp Design.—As stated already, the efficiency (in lumens per watt) of a lamp depends, other things being equal, on the operating temperature of its filament. The lamp fails because of evaporation of the filament. It is well known that in a vacuum lamp manufactured according to the best technique 10% (by weight) of the filament is lost during the normal life of the lamp. Failure is due to the differential rate of evaporation at different crystal faces. Failure ultimately occurs at some spot which is statistically ill-favoured by the coincidence of particular types of crystal boundaries. (It is an interesting fact that all filaments late in life are angular in section, due to the formation of crystal faces.) Alternatively, the lamp may be regarded as failing when so much tungsten has been deposited by evaporation on to the bulb that the blackening causes the efficiency to drop below some agreed fraction of its initial efficiency. It is therefore necessary to choose a temperature or efficiency which, within these limitations, will give a certain arbitrary life; this varies according to the type of lamp, and for ordinary lamps such as are used in lighting streets and buildings, the life aimed at is a minimum of 1,000 hours average determined on samples. To ensure this, lamp makers design for a life 20–25% longer, so as to have a factor of safety to cover errors in sampling.

In the case of certain special lamps such as those used for projection, intrinsic brightness of the light source may be of more importance than length of life. In such cases shorter lives are permissible. For example a Class A1 projector lamp having an intrinsic brightness of 2,000 candles per sq. cm. has a life of only 100 hours.

The operating temperature having been determined on this basis, the total surface necessary to give the required light output can be found. The resistance of the filament must then be chosen so that the latter shall, at the voltage on which the lamp runs, absorb the necessary energy to raise it to the requisite temperature. Finally, the resistance and surface determine the length and diameter of the wire. In the earlier tungsten lamps, as in the other metal filament lamps which preceded them, the necessary length was accommodated by arranging the wire in the form of a vertical squirrel cage, and the filament was run in a highly evacuated bulb. Its working temperature was about 2,320°K., which is very much below the melting-point of tungsten, and the obvious step for improvement which suggested itself was to replace the vacuum by an inert gas such as nitrogen which, by suppressing evaporation, would allow the working temperature, and therefore the efficiency, to be raised. Early attempts to do this failed because the heat lost by conduction and convection in the gas more than outweighed any gain which could be obtained from the higher temperature at which the filament could be run. The problem was eventually solved by Langmuir (Proc. Amer. Inst. Elec. Eng. 1913, **32**, 1915) on the following lines. The energy radiated from the surface of a filament is proportional to the area of its surface; the heat carried away by convection is also proportional to the area of the surface with which the gas comes in contact. Langmuir showed that the effective area in the second case is not that of the filament itself, but of a relatively stationary layer of gas surrounding the filament. The thickness of this layer (frequently referred to as the " Langmuir layer ") is almost independent of the diameter of the filament and is determined only by the properties of the gas. With thin filaments (such as those used for ordinary high voltage lamps) the thickness of the gas layer is greater than the diameter of the filament, so that unless a very thick filament can be used, the convection losses become great compared with the radiation. In view of the considerations which determine the diameter of the filament this discovery would by itself have been of little use, but Langmuir made a complete investigation of the behaviour of gas streams past heated filaments, out of which arose the fact that a coiled filament of fine wire would behave like a corresponding thick filament. The result of this work was the gas-filled lamp, in which the filament is a closely coiled helix running in an inert gas. Nitrogen was used in the earlier types, but owing to its lower heat conductivity, argon (containing a little nitrogen) was later substituted for nitrogen, and is now in general use. Krypton, which has a still lower heat conductivity, is better than argon, but its adoption has been limited by its high cost.

The convection losses can be cut down still further and the efficiency correspondingly raised, by increasing the size of the spiral. The limits to this are set by metallurgical considerations; a helix having a diameter more than 5 or 6 times the diameter of the wire would not be rigid enough to keep its shape at its running temperature. The effective diameter can however be increased by coiling the helix on itself. For ordinary size high-voltage lamps the gains range from 20% for a HV 40-W. lamp down to 12½% for a HV 100-W. lamp.

The change from the straight filament to the spiral form had marked consequences on the technique of tungsten filament manufacture, and these will be treated in a later section.

Manufacture of the Filament. (*a*) *Preparation of Tungsten Oxide.*—The successful manufacture of tungsten filaments depends entirely on the possibility of producing a metal of a very high order of purity; and although, as will be seen later, the presence of small amounts of materials other than tungsten is necessary at certain stages, it is essential that their nature and quantity shall be under the most rigid control.

There are many different ways of preparing tungsten oxide of the necessary degree of purity; the various countries and factories have their own preferences. It is not possible here to describe in full more than one typical process, with an indication as to the most important type of variation; to follow the variations in close detail it is necessary to study the extensive patent literature.

The source of the tungsten used in filament manufacture is either wolframite or scheelite; in European countries the latter is favoured, while wolframite is largely used in the United States. Provided the appropriate purification methods are followed, both are equally satisfactory. Wolframite $(FeMn)WO_4$ is usually decomposed by heating with strong caustic soda or potash in steel tanks (Smithells, " Tungsten," London, 1936, p. 11); typical proportions are 1,400 kg. ore, 750 kg. caustic soda and 1,800 litres water; the mixture is stirred and boiled for several hours. It is then diluted to about twice its volume and filtered, the tungstic acid is recovered preferably by precipitation with excess of calcium chloride solution to form calcium tungstate. The tungstic acid is recovered by running the tungstate sludge into boiling hydrochloric acid (equal parts commercial acid and water). Subsequent purification of the crude tungstic acid is on the lines given below for the scheelite process.

When scheelite $(CaWO_4)$ is used as raw material, it is decomposed by heating with strong commercial hydrochloric acid; the tungstic acid is left as a yellow sludge,

$$CaWO_4 + 2HCl = CaCl_2 + H_2WO_4.$$

A. Scheelite.
Decompose with HCl.
↓
B. Crude H_2WO_4 (paste).
Extract with ammonia and evaporate solution.
↓
C. Ammonium paratungstate crystals decomposed by HCl.
↓
D. Partly purified H_2WO_4 (paste) dissolved in KOH.
↓
E. Potassium tungstate solution decomposed by HCl.
↓
F. Pure H_2WO_4 (paste), washed clean and centrifuged.
Dope added (*e.g.* alkaline silicate).
↓
G. H_2WO_4 (paste) dried, groun and dsifted. The resulting WO_3 is ready for reduction.

Note.—Remaining WO_3 in mother liquor precipitated as $CaWO_4$ by addition of $CaCl_2$ and returned to A.

TABLE 1.

For the purpose of illustration, the preparation of the oxide from scheelite will be described in detail (*see also* Table 1). Commercial hydrochloric acid is heated to 70°C. in a steam-jacketed pan of any suitably resistant material, *e.g.* rubber-lined steel, and scheelite, ground to 120 mesh, is added slowly by hand in the proportion of 5 kilos scheelite to each 6 litres of acid. After all the ore has been added, the temperature is maintained at 70°C., for a total time of 8 hours. The sludge of tungstic acid is allowed to settle, and is then washed four times by decantation with boiling water, and finally once with cold water. The excess of water is drawn off, and the tungstic acid passes as a sludge or paste to the purification process (Table 1, B to G). The product from 150 kilos scheelite is dissolved in 95 litres ammonia, somewhat diluted with water. When solution is complete, water is added to bring the sp.gr. to 1·12, and the liquid is allowed to stand until the sediment (mainly lime and silica) has settled out. The clear liquor is run off into steam-jacketed enamelled iron crystallising pans, and evaporated down to about one-third of its bulk; the crystals which have the composition $5(NH_4)_2O, 12WO_3, 5H_2O$ are removed from time to time to a vacuum filter, washed with distilled water and dried at 80°C. (Fig. 1, B).

The mother liquor is treated with sufficient calcium chloride to precipitate all the remaining tungsten as calcium tungstate, and this is subsequently retreated as described for scheelite. The crystals from several batches are bulked together for the next stage (Fig. 1, C). Pure hydrochloric acid, diluted with 1½ times its volume of water is heated in a steam-jacketed pan, and the crystals added slowly by hand, in the ratio 2 kilos crystals to 1 litre strong acid. The mixture is kept boiling for 1½ hours, with constant stirring, and is then allowed to settle; the tungstic acid sludge is well washed with boiling water and after a final settling it is dissolved in caustic potash solution which is added slowly, with constant stirring. Approximately 1 kilo of potash is required for each 2 kilos of ammonium tungstate crystals originally used, and this is dissolved beforehand in about its own weight of water. The potassium tungstate is siphoned off into an iron tank, diluted to a sp.gr. of 1·12 and allowed to settle.

Final Decomposition.—The potassium tungstate solution is run into a large excess of boiling pure hydrochloric acid diluted to a sp.gr. of 1·12; about 2½ times as much hydrochloric acid is allowed as was used in the decomposition of the crystals.

The sludge of pure tungstic acid is transferred to a rubber-lined vat; the acid is siphoned off and the sludge washed 4 times with distilled water. This operation takes several days for a large batch (equivalent to perhaps 70 or 80 kilos dry WO_3), and at the end of it the slurry is centrifuged in a rubber-lined hydro-extractor down to an H_2WO_4 content of 55–60%.

Before centrifuging, it is usual to examine the sludge for such impurities as alkalis. This is done by volatilising the WO_3 in chlorine, the impurities remaining behind.

The paste from the hydro-extractor is made into a slurry with distilled water, and appropriate additives (*see later*) are introduced. Typical ones are mixed alkali silicates, equivalent to 0·4% SiO_2, 0·3% KCl and 0·2% $NaCl$. The slurry is dried in glass-lined evaporating pans, and then ignited in silica trays in a muffle to 300°C. It is finally ground in an edge-runner mill and sifted through fine bolting silk.

An alternative process sometimes used is indicated diagrammatically in Table 2. In this, the purification is effected by treatment of the ammonium tungstate solution with such reagents as magnesium chloride (to remove arsenic) and ammonium sulphide (to remove iron). The tungsten is then precipitated as calcium tungstate by the addition of calcium chloride; and the tungstate converted (by acid decomposition and ammonia treatment) back into pure ammonium tungstate which is dried and ignited to WO_3.

Solution as at B in Table 1.
↓
Add magnesium chloride and filter.
↓
Add ammonium sulphide and filter.
↓
Add $CaCl_2$ sufficient to convert all the WO_3 to $CaWO_4$.
↓
Decompose $CaWO_4$ as at A in Table 1.
↓
H_2WO_4 paste extracted with ammonia and the solution evaporated down to crystals.
↓
Crystals decomposed by heat to oxide, WO_3, which is doped, and then dried, ground, sifted and reduced to metal.

TABLE 2.

It will be seen that the greatest precautions are necessary to obtain an oxide of the necessary degree of purity; above all, it is desirable to remove compounds of titanium and iron. For this purpose, it is particularly important that the precipitation from the potash solution shall be done by pouring the alkaline tungstate solution into the acid in a fine stream, and not *vice versa*. In this way the risk of occlusion of soluble impurities is greatly diminished. The temperatures and concentration of the solutions are also important, as they influence the grain size of the oxide and subsequently the grain size of the reduced powder. The latter largely decides the suitability of the finished metal for use in lamps, and while the control is mainly exercised in the next process (reduction), it is necessary to maintain rigid standardisation of whatever processes are used for the preparation of the oxide so as to eliminate as far as possible at least one variable factor.

Reduction of the Oxide to Tungsten Powder.—The reduction is usually carried out in two stages. The oxide is contained in small iron boats which are pushed along iron tubes about 2 in. diam. and 20 ft. long. In the first stage the tubes are heated in definite zones to temperatures ranging from 500°C. at the beginning to about 750°C. at the end. The time taken is of the order of 2½ hours. The second stage is similar, but the temperatures are considerably higher. A continuous flow of dried electrolytic hydrogen is maintained through the tubes, the gas passing through driers in a closed circuit. The purity and dryness of the hydrogen are important. The rate of flow is strictly controlled, since this, and the rate of heating as well as the dryness of the hydrogen, determine the grain-size distribution of the metal.

The metal powder after reduction is accumulated in large batches and sieved.

Experience has shown that to obtain a metal which is satisfactory both from the point of view of working properties and behaviour in lamps, certain grain-size distributions are necessary. The grain-size distribution is therefore controlled by actual measurement on samples

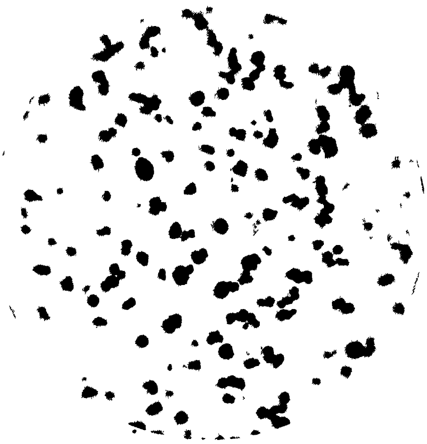


FIG. 1.

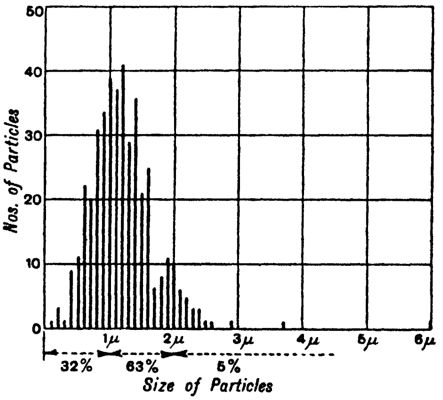


FIG. 2.

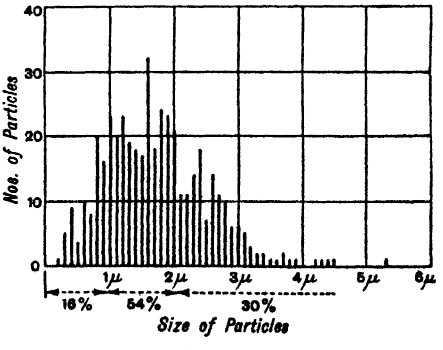


FIG. 3.

taken from the large batches. These samples are rubbed out with turpentine on slides and photographed at a magnification of 500 (Fig. 1).

The negative is projected at a magnification of 50 on to a screen; the numbers of particles within definite ranges are counted, and distribution diagrams are plotted. Figs. 2 and 3 show typical bad and good distributions. In the latter case, the powder concerned had a size distribution from 0·2μ to 5μ with a maximum at about 1·5μ. If the distribution is unsuitable, a wire made from the powder may have either bad working qualities or a poor life-behaviour in lamps.

Conversion of the Metal Powder to Wire. (*a*) *Pressing.*—The powder is placed in a steel mould and pressed into a coherent rectangular bar. The pressure is applied to the long side of the bar, and for a bar 30 cm. × 1 cm. × 1 cm. is usually about 2,000 kilos per sq. cm. (12·5 tons per sq. in.).

(*b*) *Pre-sintering.*—The fragile pressed bar is carefully transferred on a tungsten boat to a tube furnace in which it is heated in a stream of hydrogen to 1,100°C. for 20–30 minutes. Under these conditions probably very little if any grain-growth occurs, but the bar becomes strong enough to stand handling in the next process.

(*c*) *Sintering.*—The hardened bar is fixed vertically between two clamps, the lower of which floats in a water-cooled bath of mercury, the upper one being fixed to a water-cooled support. A water-jacketed copper housing is lowered over the assembly, and hydrogen is allowed to flow downward through it at a rate of 300 litres per hour; the joint at the bottom is made by a mercury seal (*see* Fig. 4). A current is passed through the bar to heat it, and is gradually increased over a period of 15 minutes to a maximum at which it is maintained for another 15 minutes. The current is usually controlled by some form of induction regulator. The appropriate maximum current is determined for any particular batch of metal by finding the current required to fuse it under ordinary sintering conditions; a certain fraction of this current is adopted as a working maximum; the fraction ranges from 88 to 95%; for a bar of the size described (*i.e.* pressed originally to 30 cm. × 1 cm. × 1 cm.) the current is in the region of 2,700 amperes. This corresponds to a temperature of about 3,100°C. (about 3,370°K.; the accepted fusing temperature is 3,655°K.).

During the sintering process, rapid grain growth takes place in the bar, and this is aided by the temperature gradient between the ends and middle of the bar, and between the centre and outside. Considerable shrinkage takes place (linear shrinkage of 15–20%). The density of a sintered bar is about 16·8 gm./cm.^{3}. Any impurities in the tungsten are also volatilised in this process, and this is aided by the "additives" or dope, such as alkaline silicates, which were introduced into the oxide. The exact mechanism of this action is undecided; possibly the vapour of the additives carries away other impurities, or possibly they act by leaving interstices through which these can escape.

The exact grain size of the sintered bar is not of vital importance to its subsequent behaviour, but it is important that it should be under control, otherwise adjustments would be necessary in the later working processes. The figure commonly aimed at is about 1,500–2,000 grains

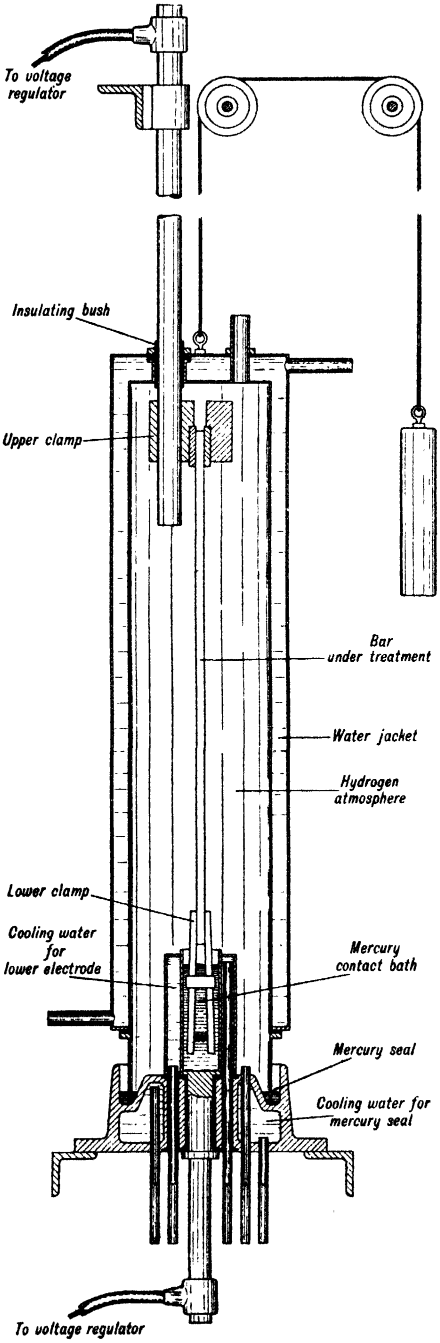


FIG. 4.

per sq. mm., and Fig. 5 shows an etched section of such a bar and Fig. 6 a very coarse bar. Grain counts are taken as a routine in manufacture.

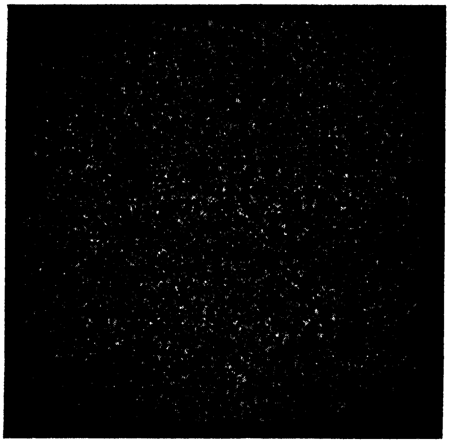


FIG. 5.

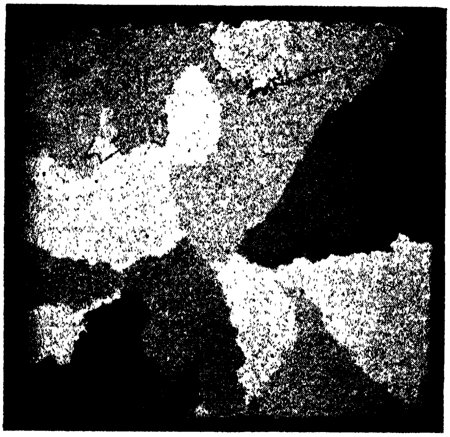


FIG. 6.

Swaging.—A sintered bar cannot be drawn into wire until the crystal structure has been broken down by hot hammering, or " swaging." In the swaging machine (Fig. 7), a pair of hammers or dies are rotated and are forced apart and together in rapid alternations while the bar or rod passes through them. Before swaging, the unsintered ends of the bar are cut off, and the bar heated in hydrogen in a tube furnace to a temperature of nearly 1,500°C. In the early stages of swaging, a little over half the bar is swaged at a time, and the bar is reversed and reheated before completing its passage through the hammers. When the diameter has been decreased to about 5 mm. the bar is transferred to other swaging machines through which it passes directly, being heated by a gas furnace placed just in front of the hammers. Swaging is continued with a total of about 25 steps to a diameter of about 1·5 mm., and during the process the rod is reheated to a temperature of about 2,100°C. once or twice in a sintering machine to allow of further grain growth taking place after the voids in the original bar have been closed by the hammering.

The swaging temperatures are gradually dropped as the size of the rod is reduced, and are adjusted so as to be below the recrystallisation temperature at each size. The final temperature is about 1,100°C. Fig. 8 shows the structure of a swaged rod 2 mm. in diameter, from which it can be seen how the grains have become elongated and are gradually becoming fibres.

Wire Drawing.—The swaged rod (diam. 1·5 mm.) is hot-drawn through dies; in the earlier stages (down to about 0·5 mm.) dies of tungsten carbide are used. From this size downward diamond dies are used. The wire is lubricated by means of colloidal graphite to minimise wear on the dies, and is heated by means of a row of gas flames placed just before the die. To enable the wire to be threaded through the die, it is pointed by dipping into fused sodium nitrite. The smallest wires normally used in lampmaking have diameters of the order of 0·01 mm. The diameter is usually calculated from the weight of a known length of wire, the density assumed for this purpose being 19·35.

The shape of the die needs careful control, since it is one of the important factors in maintaining uniformity in the filament and therefore in the finished lamp. Fig. 9 shows magnified sections through good and bad dies of about 0·025 mm. diam., and gives an idea of the accuracy which is demanded.

COILING OF THE FILAMENT.—The production of filaments in the form of a helix demands the utmost precision, since errors in the dimensions of the helix have serious effects on the behaviour of the lamp. This is dealt with in the next section.

Coiling.—The coiling operation is performed by automatic machinery, the general principle being that a mandrel wire is drawn slowly through a nozzle, while a spool of wire rotates about it, producing a helix. The tungsten wire is usually cleaned before this operation to remove adhering tungstic oxide and graphite. This may be done either by various electrolytic methods, or more simply by passing the wire through a bath of hot caustic soda solution and scrubbing off the loosened graphite with suitable pads. The mandrel is made of either soft iron or molybdenum. The latter is used when the coils are to be subjected at a later stage to high temperature treatment. Molybdenum wire is manufactured both for this purpose and for use in filament supports by methods very similar to those described above for the tungsten filament.

For lamps of the coiled-coil type, the primary helix is wound in a continuous length, and is then treated exactly like the original wire in other coiling machines of a special type; that is, the primary helix, on its mandrel, is wound round a secondary molybdenum mandrel, pro-

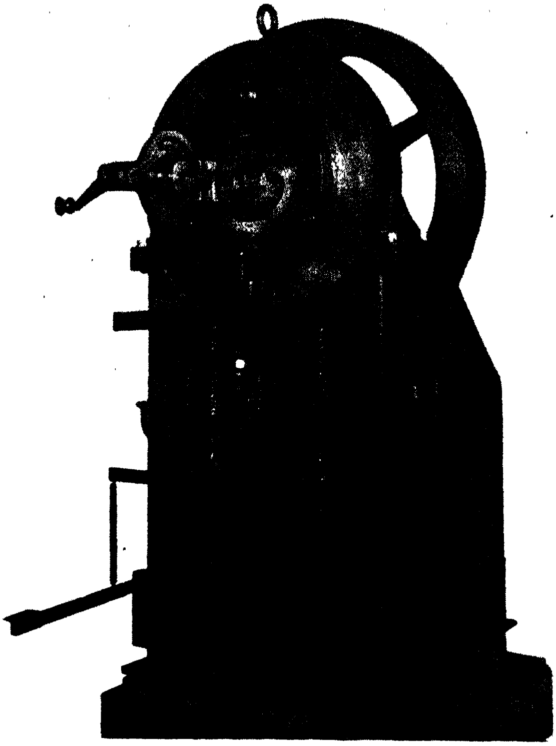


Fig. 7.

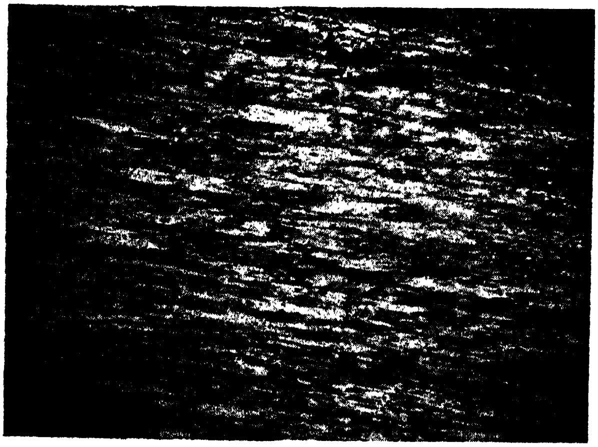


Fig. 8.

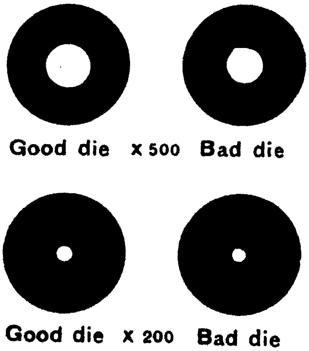


Fig. 9.

ducing the coiled coil. During the secondary coiling, the machine automatically spaces the coils at intervals, so as to leave a straight portion of single helix at which individual filaments can be cut off ready for mounting in the lamp. After coiling, the filaments are heat-treated at such a temperature that they will retain their shape when the mandrels are removed. The temperatures used vary over a wide range according to the size of filament and type of wire used. In general, for coiled-coil filaments, temperatures well above 1,000°C. are necessary.

The mandrels are dissolved out in an acid bath; hydrochloric acid is used for iron mandrels, and a mixture of nitric and sulphuric acids for molybdenum.

The filaments are thoroughly washed to remove acid, treated with a caustic solution to remove traces of oxide, and finally washed in distilled water and dried.

Precision in Filament Manufacture.—Although this is primarily an engineering matter, it needs mention here, since it is a fundamental problem in the manufacture of filaments. Lamp manufacture is an example of highly developed mass production, and the standards of uniformity in the finished product are very exacting. The wire used in lamps for general lighting service ranges in diameter from 0·0135 mm. to 0·435 mm. In order to maintain a satisfactory life performance, the wires must be accurately round, and the local variations in diameter must not exceed 0·5–1% according to the size of the wire. The diameter of the mandrel wire needs correspondingly close control, as do also the pitch of the helices and the tension of the wire during coiling.

The Behaviour of the Filament in the Lamp.—The filament before it is burnt at its operating temperature in the lamp has a fine fibrous structure. On heating, the fibres break down, and in the neighbourhood of 2,000°C. are converted into small equiaxed grains, and grain growth then proceeds, the larger grains absorbing the smaller. The temperatures at which these changes take place depend on the exact composition of the wire. In the straight filaments which were employed in the earlier types of vacuum lamp, this process is liable to lead to the formation of grain-boundaries occupying the whole diameter of the wire, and these constitute a source of weakness, since the crystals tend to flow at the boundaries and the wire ultimately breaks (this is known as "off-setting"). Earlier efforts to avoid this included the addition of about 0·75% of thoria, which restrains the grain growth and greatly diminishes the risk of off-setting.

Another line of attack was to produce filaments in which exaggerated grain growth could take place, so that the whole filament would consist of very few crystals, or even of a single crystal, thus minimising the danger by reducing the number of grain boundaries.

This problem arose anew with the introduction of coiled filaments for gas-filled lamps. The difficulty here was not so much the breaking of the filaments as the fact that as grain growth proceeded throughout the life of the lamp the movements at the grain boundaries caused the spirals to sag and open out, leading to a rapid falling off in the efficiency of the lamp due to high gas losses. The first remedy attempted was to restrain grain growth by the use of thoria (again about 0·75%). Fig. 10 shows a section through the coils of such a filament after long burning; the comparatively small size of the grains is contrasted with the large grains in a filament made from "pure" tungsten. The method adopted at the present day is to make use of exaggerated grain growth, which is achieved (under suitable heat-treatment) by the use of additives such as alkaline silicates. Numerous combinations have been used and are in use at the present day; a typical one was mentioned earlier in the description of metal making. These additives, as already stated, cannot be detected by the usual analytical or spectroscopic means after the sintering process, but they have a profound effect on the grain-growth of the coiled filament when heated. The process is completed in the time taken for the

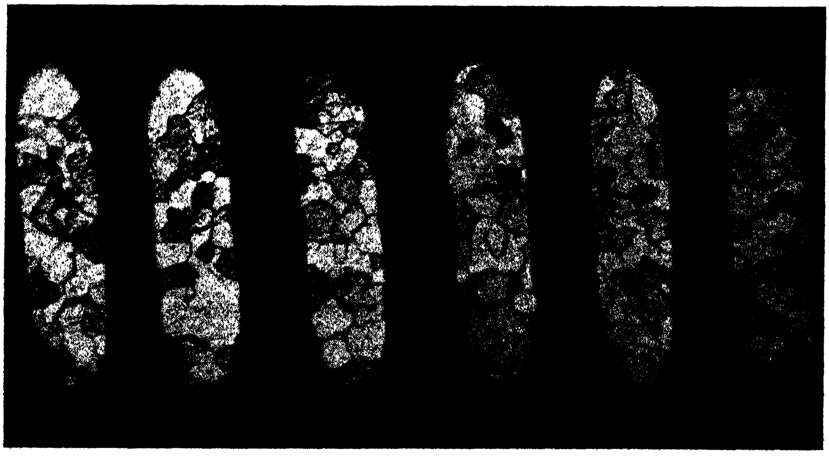


Fig. 10.

filament to reach its operating temperature, and the filament is left in a stabilised state in which the individual crystals occupy several turns of the spiral (*see* Fig. 11).

Examination of Filaments.—The preparation of specimens showing the structure of filaments is of importance, since it is in regular use for control purposes. The filament is embedded in a low melting lead-borate glass containing manganese (to give it a dark colour for ease in photography). The glass is held in a groove cut in a brass block; it is melted and the filament dropped on to its surface. For the examination of coiled filaments (which is mostly required), the block is ground down until a section through the upper part of the spiral is exposed as a series of lozenges. After polishing, the tungsten surface is etched by means of boiling 3% hydrogen peroxide or a cold solution containing equal volumes of 10% caustic soda and 30% potassium ferricyanide.

Tungsten rods or bars are usually mounted for examination in solder contained in a brass cup.

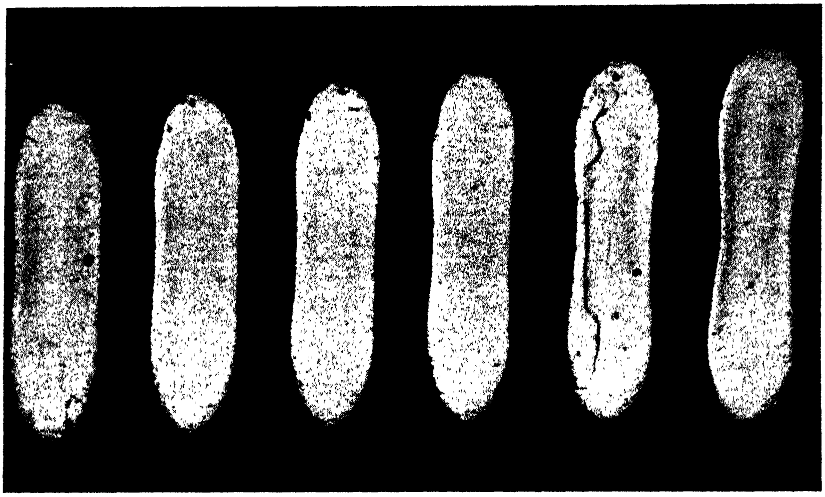


Fig. 11.

Carbon Filaments.—Although carbon filament lamps are no longer in normal use for lighting purposes, they are still made for a few special purposes. They form a convenient and cheap type of resistance; they are also used as radiators for medical purposes, and to a small extent as room-heating radiators and for other heating purposes. Carbon lamps of high ratings (30–50 candle power) are still used where extreme resistance to shock is important.

A typical standard process used in the manufacture of carbon filaments is the following:

The raw material is pure white blotting paper, which is dissolved in a strong solution of zinc chloride, forming a viscous syrup. This is squirted through a glass die into alcohol acidified with hydrochloric acid; the cellulose is regenerated in the form of a continuous thread. After being left to harden for some days the thread is washed repeatedly to free it from zinc chloride, and it is wound on a large drum to dry. The tough dried thread which looks like a violin string is set to its desired shape on a carbon former, and in this state is heated in a crucible to a temperature of 1,500°C. During this operation, oxidation is avoided by packing the filaments, on their formers, in graphite powder.

After carbonising, the filaments are mounted on nickel support wires with hollowed ends, and the joint completed by depositing carbon from a hydrocarbon bath in which they are immersed while a current is passed. In order to ensure that the filament shall be uniform in diameter, it is heated by a current in an atmosphere of heavy petroleum vapour. The thinner parts of the filament heat up more than the rest, and so receive a thicker deposit of carbon from the vapour.

This operation is of classical interest, and is known as "flashing." The filament is now in a state ready for use; its diameter is uniform and its surface is covered with a thin hard layer of deposited carbon.

Filaments for Thermionic Valves.

(1) *Tungsten.*—Tungsten filaments are used at the present day only in the largest transmitting valves, and the method of manufacture is as described for lamp filaments.

(2) *Thoriated Tungsten.*—The manufacture of this material is similar to that of ordinary tungsten, except that sufficient thorium is added to the oxide (usually in the form of thorium nitrate) to give the equivalent of about 0·7% of thoria in the finished wire.

Thoriated tungsten filaments are used for small transmitting valves, and also of a few special types of receiving valves. During the manufacture, the filament is "activated" by a process which causes an approximately monatomic layer of thorium to be formed on the surface. For this purpose the filament is heated for a short time to a high temperature (ca. 2,800°K.) to reduce some of the thoria, and then held at a somewhat lower temperature to stabilise the emission.

(3) *Oxide-Coated Cathodes.*—These are of a different type from the valve filaments described above, and consist essentially of a metallic filament, coated with a thermionically active material. The filament acts as a heater, and is usually made of nickel, although tungsten and platinum are also used. The coating most generally used is a solid solution of barium and strontium oxides in approximately equimolecular proportions; it is actually applied in the form of a mixture of the precipitated carbonates and converted into oxides by heating *in situ* to a temperature round about 1,400°K.

TABLE 3.—DATA ON OPERATING TEMPERATURES AND EMISSION PROPERTIES OF THE THREE TYPES OF FILAMENTS.

Filament (or cathode).	Operating temperature.	Emission.	Emission efficiency.	Remarks.
Tungsten	2,500°K.	275 mA/cm.^{2}	3–5 mA/watt	
Thoriated tungsten. .	1,900°K.	3,000 mA/cm.^{2}	20–25 mA/watt	The emission is more sensitive to poisoning by oxygen and water vapour than that of pure tungsten.
Oxide-coated (BaSr) .	1,040–1,100°K.	250–400 mA/cm.^{2}	150–250 mA/watt	Very sensitive to poisoning by oxygen and water vapour.

Bibliography.—F. Rodet, "Les lampes à incandescence électrique," Paris, 1907; Langmuir and Orange, Tungsten Lamps of High Efficiency, Trans. Amer. Inst. Elec. Eng. 1913, **32**, 1895; C. Weber, "Die elektrischen Metallfadenglühlampen," M. Jänecke, Leipzig, 1914; B. P. Dudding and C. J. Smithells, The Development of the Electric Incandescent Lamp, Beama, 1923, **13**, 221; B. Duschnitz, 125 Jahre elektrisches Glühlicht, E.T.Z. 1928, **30**, 1111; Assocn. of Edison Illuminating Cos., The Development of the Incandescent Electric Lamp up to 1879, Trans. Illum. Eng. Soc. 1929, **24**, 717; G. Chelioti and B. P. Dudding, Precision in Incandescent Lamp Manufacture, G. E. C. Journal, 1931, **2**, 103; C. J. Smithells, "Tungsten," Chapman & Hall, London, 1936.

L. D. G.

FILBERT. The nuts are the seed of *Corylus* spp. usually designated *C. avellana* L. Other species and hybrids (including cobs) are *C. pontica* Koch, and *C. maxima* Mill. American species of hazelnuts are given as *C. rostrata* Ait. and *C. americana* Walt.

König ("Chem. Mensch Nahr.-Genussm." 1903, **1**, 611) gives the composition of the kernels as:

H_2O.	Protein.	Fat.	N-free extract.	Ash.
7·1	17·4	62·6	10·4	2·5%

Bertram (Öle, Fette, Wächse, 1936, No. 14, 2–4) reports the following characteristics of the French oil: d_{20}^{20} 0·9144, n_D^{28} 1·4691, iodine value (Hanus) 86·8, saponification value 192·0, unsaponifiable matter 0·35%. The oil contains 8% of saturated acids, largely palmitic. The unsaturated fraction includes oleic acid 78·2 and linoleic acid 9·1%.

Osborne and Campbell (Connecticut Agric. Exp. Sta. Rept. 1895, 288) describe the isolation from the nuts of a globulin, *corylin*, C 50·7, H 6·86, N 19·17, S 0·83, O 22·42%. The N distribution of corylin, according to Osborne and Harris (J. Amer. Chem. Soc. 1903, **25**, 323), is total N 19%, basic N 5·75, non-basic N 10·7, N precipitated with MgO 0·16, ammoniacal N 2·20%. The constituent amino acids of corylin include cystine 1·5 and tryptophan 2·86% (Jones *et al.* J. Biol. Chem. 1924, **62**, 183).

A. G. Po.

FILICIC ACID *v.* FILIX MAS.

FILICIN *v.* FILIX MAS.

FILICITANNIC ACID *v.* FILIX MAS.

FILITANNIC ACID *v.* FILIX MAS.

"*FILITE*," ITALIAN (Vol. IV, 519*a*).

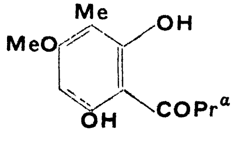
FILIX MAS.—Filix mas (B.P.), Aspidium (U.S.P.), Male fern; *Rhizoma filicis* (*Racine de fougère male* (Fr.); *Wurmfarn, Johanniswurzel* (Ger.). The rhizome of male fern, ***Aspidium filix mas*** (Swartz) or ***Dryopteris Filix-Mas*** Linn. (Schott) has been a favourite anthelmintic medicine since the times of Theophrastus, Dioscorides, Pliny, and Galen. For botanical characters, *see* Woodville (Med. Bot. 271), Moore and Lindley (Ferns of Great Britain, 14–17), and Bentl. and Trim. 300; *cf. also* Czapek: "Biochemie der Pflanzen," 1925, vol. III, pp. 565. ***Filix mas*** (Fam. Polypodiaceæ) is indigenous to all Europe, North Africa, North Asia, Himalaya and America from the North as far South as Peru.

The early chemical investigations of the rhizome (*see* Pereira, Mat. Med., 3rd ed. 1853, II, 959, and Poulsson, Arch. exp. Path. Pharm. 1891, 29, 1) show, that besides the constituents common to plants, it contains a peculiar ***green fixed oil***, tannin and a crystalline compound, first analysed by Luck (Jahrb. prakt. Pharm. 1851, **22**, 129) and named by him *filicic acid* (also called *filicin*). These constituents are all found in the ethereal extract of "oil of male fern" (Oleoresina Aspidii) in which form alone the drug is made use of in medicine. Oleoresina Aspidii must contain 24–26% (B.P.) or not less than 24% (U.S.P.) of filicin. The rhizomes must not be used later than one year from the date of collection, careful drying is essential. *Cf.* articles on *Filix mas* and *Extr. filicis* in B.P. 1932, and on *Aspidium* and *Oleoresina Aspidii* in U.S.P. XI (1936). The green fixed oil is composed, according to Katz (Arch. Pharm. 1898, **236**, 655), of the glycerides of oleic, palmitic and cerotic acids, the chief constituent being triolein. The tannin, *filitannic* or *filicitannic acid* is, according to Malin (Annalen, 1867, **143**, 276), a glucoside (*see also* Arch. Pharm. 1906, **244**, 466).

Filicic acid, $C_{35}H_{42}O_{13}$ (Poulsson, Chem. Zentr. 1891, II, 673) or $C_{35}H_{38}O_{12}$ (Boehm, Annalen, 1901, **318**, 256). Poulsson states that the physiologically active substance is a colourless amorphous powder, melting at about 125°. In boiling ethereal solution it is converted to its lactone *filicin*, $C_{35}H_{40}O_{12}$ or $C_{35}H_{38}O_{12}$. This anhydride is inert and forms yellow rhombic leaflets, m.p. 184°. It is insoluble in water, sparingly soluble in cold EtOH, readily in hot. By careful treatment with alkali it can be retransformed to the active acid. These results do not agree with those of Boehm, who obtained a crystalline filicic acid in a yield of 3·5% by merely recrystallising the amorphous substance from acetone, mp. 184–185°, easily soluble in $CHCl_3$ and CS_2, soluble in C_6H_6. Prolonged heating in alcoholic solution causes destruction of the filicic acid molecule and *albaspidin* (*see* later) is eventually isolated (Boehm, Annalen, 1901, **318**, 268).

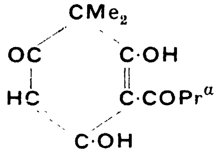
An insight into the constitution of filicic acid has been obtained by Boehm, who isolated a number of other crystalline substances from fern extracts, and has made by far the most important contributions to our knowledge of the subject. (Arch. exp. Path. Pharm. 1897, **38**, 35; Annalen, 1898, **302**, 171; 1899, **307**, 249; 1901, **318**, 230, 245, 253; 1903, **329**, 269, 310, 338). All the substances isolated by Boehm appear to be either methylated phloroglucinyl propyl ketones, or to consist of two or three such nuclei joined together by one or two methylene groups. Boehm also gives a speculative formula for filicic acid, according to which the acid is a combined di- and triphenyl derivative.

Aspidinol, $C_{12}H_{16}O_4$, bright yellow crystals, m.p. 156–161°, is the simplest of these substances. For its preparation, *see* Annalen, 1901, **318**, 247. By digesting aspidinol with zinc-dust and NaOH for ten hours, it is decomposed to methylphloroglucinol monomethyl ether and *n*-butyric acid. It has the constitution:



By the condensation of C-methylphloroglucinol β-methylether and *n*-butyronitrile Karrer and Widmer (Helv. Chim. Acta, 1920, **3**, 392) obtained two isomeric ketones, one of which was identical with aspidinol (*cf. also* Robertson and Sandrock, J.C.S. 1933, 819).

Filicin (filicic acid), on the other hand, is the most complex, and consists of three such ketone nuclei as mentioned above. On boiling filicin for a short time with zinc dust and NaOH (Annalen, 1901, **318**, 236), it yields, amongst other products, "*filicinic acid butanone*," m.p. 95–97°, which is isomeric with aspidinol and has the constitution



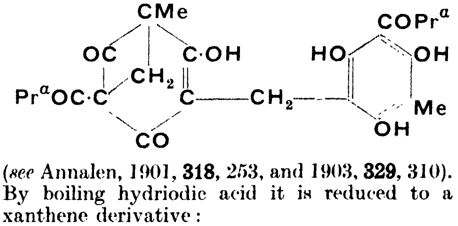
or is tautomeric with it. By more prolonged boiling it breaks up into *n*-butyric acid and *gem*-dimethylphloroglucinol (*filicinic acid*), m.p. 212–215° (*see* Annalen, 1899, **307**, 249). The latter substance gives, on oxidation, dimethylmalonic acid. For the synthesis of filicinic acid, *see* Robertson and Sandrock, J.C.S. 1933, 1617.

The other substances isolated by Boehm are composed of two ketone nuclei joined by one methylene group.

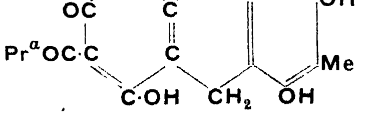
Albaspidin, $C_{25}H_{32}O_8$, needles, m.p. 151–152°, consists of two filicinic acid butanone residues, and can be synthesised from this ketone by means of formaldehyde, the methylene-bridge being in meta-position of both butyroyl-groups (*see above* filicinic acid butanone, and *also* Boehm, Annalen, 1901, **318**, 305).

Phloraspin, $C_{23}H_{28}O_8$, colourless needles, m.p. 211°, is similarly built up of methylphloroglucinol-*n*-butanone, and the methyl ether of phloroglucinol-*n*-butanone, which are two isomeric ketones, $C_{11}H_{14}O_4$, lower homologues of those already referred to (Annalen, 1903, **329**, 338).

Flavaspidic acid, $C_{21}H_{28}O_8$, is a strong acid which decomposes carbonates with evolution of CO_2. It exists in two modifications, melting at 92° and 156°, and appears to have on one side a four-membered ring:

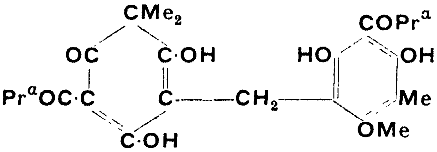


(*see* Annalen, 1901, **318**, 253, and 1903, **329**, 310). By boiling hydriodic acid it is reduced to a xanthene derivative:



m.p. 257–259°. With the exception of filicic acid, all the above substances occur also in the rhizome of *Aspidium spinulosum* (Swartz), in which the filicic acid is replaced by ***aspidin***, $C_{25}H_{32}O_8$, m.p. 124·5° (*polystichin*, Poulsson, Arch. exp. Path. Pharm. 1898, **41**, 246).

As the latter fern is often confused with *A. filix mas*, the commercial extracts of the male fern may contain aspidin as well. The substance may be recognised in the crude extract by crystallisation (Hausmann, Arch. Pharm, 1899, **237**, 544; Annalen, 1903, **329**, 321). Aspidin has most probably the constitution:



being built up of aspidinol and filicinic acid butanone.

Most of the above substances are physiologically active on tape worms and other lower animals (Boehm; Straub, Arch. exp. Path. Pharm. 1902, **48**, 1); the simplest one having any degree of activity is filicinic acid butanone; lower degradation products are inactive. It is difficult to attribute the anthelmintic action to any one substance in particular, but according to Kraft (Arch. Pharm. 1904, **242**, 489) this action is primarily due to yet another substance, *filmarone*, more complex than any isolated by Boehm.

Kraft states that good extracts of male fern contain 3·5% filicic acid, 2·5% flavaspidic acid, 0·05% albaspidin, 0·1% aspidinol, 0·1% flavaspidin (probably identical with phloraspin of Boehm) and 5% of filmarone. The last substance, $C_{47}H_{54}O_{16}$ or $C_{47}H_{52}O_{16}$, is an amorphous brownish-yellow acid, melting at about 60° and containing four different phloroglucinyl ketone groups. Boiling with zinc-dust and $NaOH$ decomposes it into filicic acid, aspidinol and various other substances (*see* Kraft, *l.c.*). Whether filmarone is a chemical individual is not clear, but it seems to have met with a certain measure of clinical success.

For cases of poisoning by fern extracts, *see* Poulsson (Arch. exp. Path. Pharm. 1891, **29**, 1); for detection of filicic acid in such cases, *see* Bocchi (Chem. Zentr. 1896, II, 1137). Müller and Kofler (Arch. Pharm. 1930, **268**, 644) describe biological tests on fish and give literature references (*see also* Chem. Zentr. 1929, I, 118). For anthelmintic and haemolytic action of products of *filix mas*, *see* Jodlbauer, Arch. exp. Path. Pharm. 1932, **164**, 457.

G. B.

FILMARONE *v.* Filix Mas.

FILTER PAPER. Filter papers of all grades and for every purpose are now available of British origin as a consequence of administrative action, devised to counter the menacing inconveniences experienced during the war (1914–18), before which period filter papers were largely or, in some of the most important grades, exclusively of foreign origin. Thus, qualitative, quantitative, ash-free, fat-free, soft and tough grades are available, and some are also sold moulded thimble-wise, for Soxhlet extractions, as well as in the usual sheets and/or discs. All are made from purified cellulose of adequate strength, to suit a wide range of purposes. These purity and strength requirements, plus filtration velocity, in practice can be fulfilled only by employing cotton and linen, separatedly or mixed, as raw materials; other materials have shorter fibres and are not easily purified from minute quantities of undesirable impurities. Both cotton and linen have the fibre length necessary and, hence, both will supply the strength required with even a minimum of hydration in the paper-maker's beater (*v.* Cellulose, Vol. II, 460*b*), and, thus, maximum filtration velocity can be conserved. The operation of beating allows hydration and, therefore, strength to be accurately controlled, other methods of hydration with reagents are not employed, because the subsequent removal of traces of the reagents is difficult and the action of the beater is far more easily controllable in their absence.

For the best grades, new cotton and linen cuttings are the raw materials; the cellulose is then free from its common degradation products and, also, almost free from inorganic matter. Particularly, it is free from lime salts present in old rags, derived from hard waters in laundering, and from iron, copper, alumina and silica. Organic matter present may be, in old rags cellulose degradation products and starch, fats, oils and resins, in new rags a minute trace of fatty or resinous matter which normally occurs in the living plant. For some special purposes a fat-free paper is essential and even for use with aqueous reagents it is advantageous because water will not otherwise wet evenly and with maximum rapidity and hence velocity of filtration will be diminished. A clean surface of distilled water is contaminated by contact with filter paper not treated for fat removal (with alcohol–ether) so that its normal surface tension is disturbed (Rayleigh).

Industrially, the cotton and linen are boiled with weak alkali, sodium carbonate for new cuttings and caustic soda for old rags; the reagent is removed, the material then washed and centrifuged to 25–30% concentration, bleached gently with chlorine gas and thoroughly washed. Finally, it is made into paper (more correctly water-leaf), after the appropriate degree of beating and without sizing or any other added ingredient.

The normal ash-content of pure cellulose is about 0·1–0·4% and, for quantitative filter papers, this is reduced to about 0·008% by extraction in succession with HCl and with HF. The pulp after the bleaching operation is treated with 1 litre of conc. HCl/350 kg. cellulose then washed and treated with the like quantity of HF and, finally, thoroughly washed, the last traces of acid being more easily removed with the help of a minute trace of NH_3 in the wash water. This treatment with acid leads to some degradation of the cellulose by hydrolysis, and reducing substances thus formed in the paper will decolorise dilute permanganate solution (McBride and Sherrer, J. Amer. Chem. Soc.

1917, **39**, 928); the main portion is, however, extracted by the first portion of the permanganate reagent passing through.

Bibliography.—"Testing of Filter Paper" (Papier-Fabr. 1933, **31**, S116).

C. J. J. F.

"FILTROL" (Vol. IV, 248*c*).

FININGS (Vol. II, 102*a*).

FINISHING TEXTILE FABRICS. The term "finishing," as used in the textile industry, generally refers to those operations which constitute the third or final phase in the refinement and embellishment of woven and knitted fabrics. The first phase may be represented by scouring and bleaching, or preparing in the case of wool goods, and the second phase by a colouring process, *e.g.* dyeing or printing. In some cases, operations of the first and second phases are not carried out, *e.g.* the finishing of canvas linings for men's wear, cotton cloth in the grey state, etc., whilst in the production of white materials of all kinds, second-phase operations are obviously excluded. Again, in the wet-processing of crêpe cloths, the first-phase operations are essential "finishing" operations, inasmuch as the successful production of satisfactory finished effects, whether coloured or white, are almost entirely dependent on the nature of, and the care taken in carrying out, the initial treatment of the cloths. Finishing technique, therefore, is subject to wide variation and the degree of refinement and embellishment required as well as the production of other distinctive effects are determined largely by considerations of (*a*) the nature, physical alignment and/or state of the fibres in the yarns composing the fabrics; (*b*) the swelling capacity of the fibres in presence of aqueous liquids or steam; (*c*) the behaviour of the fabric material under mechanical pressure, and cutting, abrasive, tearing, frictional, etc., operations in the wet and dry states, at low and elevated temperatures; (*d*) the varying susceptibility of different fibres to modification in presence of chemical agents; and (*e*) the suitability of fibres for absorbing and/or acting as receptive media for finishing materials which are needed to impart special properties to the finished fabrics.

The spun fibres are termed "yarns" and the latter are used as warp yarns (longitudinal threads of fabric) and weft or filling yarns (threads at right angles to warp threads). Warp yarn is invariably stronger than weft yarn, whilst in so-called union fabrics, *i.e.* fabrics containing more than one kind of fibre, the yarns may be of widely different character, *e.g.* cotton warp and wool weft or composite yarn spun from a mixture of cotton and wool may be used. Yarn, itself, is sometimes subjected to finishing operations, *e.g.* wax polishing of certain types of cotton and linen thread and processes for preventing worsted yarn from felting when washed, but, in the majority of cases, finishing is concerned with the treatment of woven and knitted yarn, *i.e.* fabrics or webs. In some textile centres, the term "finishing" embraces all wet- and dry-processing operations which fabrics undergo after leaving the looms or knitting machines; it often happens, therefore, that scouring, bleaching, mercerising and even dyeing, as applied to cotton and other cellulosic fibres, are included under this term; a brief account of modern cloth mercerising is given in this article.

Apart from the points already discussed, the production of any type of finished effect is governed also by economic factors and, in particular, the uses to which the finished goods are to be put, so that, in many cases, these and other considerations have to be taken into account in designing the structures of fabrics. Moreover, the production of consistent satisfactory finished effects on all classes of fabrics is possible only by a clear understanding of the characteristic properties of the pertinent fibres and their behaviour when present in the various physical forms of the fabrics to be treated, whilst the interdependence of all operations leading to the finished material scarcely needs to be stressed.

The majority of true finishing operations can only be carried out satisfactorily in presence of moisture, heat, pressure and/or friction.

Finishing Cellulosic Fabrics.

Wet-Processing Cotton Cloth.—Before discussing the actual finishing operations to which cellulosic fabrics are subjected, it is desirable that a few brief notes regarding two important branches of wet-processing, viz. bleaching and mercerising should be recorded.

BLEACHING.

A large proportion of the world's production of finished cotton cloth is finished in the bleached and mercerised condition; also, much of it is dyed and/or printed. Bleaching has already been dealt with in Vol. II. Its object is to remove, either partly or completely, according to requirements, the natural and acquired impurities associated with the fibres. The cloth is generally bleached in rope form, although heavy cloths are often bleached in open width. Low or high pressure boiling of the cloth in alkaline liquors* (lye-boiling) effects the removal of fatty and greasy matters, etc., by a series of reactions based on hydrolysis, emulsification and dissolution, whilst oxidation of the natural colouring matters to soluble colourless products is effected subsequently by means of hypochlorites or hydrogen peroxide. In spite of the ever urgent call for speeding up production, the time-factor in the lye-boiling operation is still an exceedingly important requirement in the production of highly satisfactory goods. When caustic soda is used, it is best not to use live steam for heating and circulating the liquor; two lye-boils with soda ash, with or without a little caustic soda, give more uniform and satisfactory results than one lye-boil with caustic soda, although the general tendency at the present time is to make one high pressure lye-boiling operation with caustic soda suffice for a wide range of cloths. A preliminary boiling of the cloth in milk-of-lime (lime-boil) is still practised to a considerable extent, especially in the case of cloth which is to be printed subsequently. As regards the plant in use, it is remarkable that very few outstanding improvements have been introduced during the past 50 years. In many works, the cloth, in rope form, is directed into position (piling), in the kiers, or pits, as required, either by hand labour or by means of mechanical pilers. Boiling vessels (kiers) of the puffer pipe, injector and outside heater with centrifugal pumps are all types in use, although the most efficient type for general use is a kier built on the last-named principles.

Cotton-Staple Fibre Cloths.—Cloths containing cotton and staple fibre (rayon) yarns are less resistant to alkali-boiling than 100% cotton cloths. Consequently, in cases where it is necessary to remove natural impurities from the cotton portion, it is best to boil the goods in open vessels, since rayon fibres are quickly attacked when boiled with alkali under pressure, and the fabric may suffer a serious loss in weight. Also, all decolorising operations (bleaching) with oxidising agents should be conducted cold or only lukewarm and with great care in order to prevent degradation of the staple fibre.

MERCERISING.

Finely woven cotton cloths, either plain or with coloured stripes, intended for making up into shirts, handkerchiefs, dress materials, etc., are usually bleached and mercerised before they are subjected to the actual finishing operations. Certain classes of goods, which are to be dyed, are first subjected to a comparatively mild treatment with caustic soda in order to swell the fibres slightly and increase their affinity for dyes.

The term "mercerising" was applied originally to a process of treating cotton, either yarn or cloth, with cold concentrated caustic soda solutions in such a way that it acquired a permanent silky lustre; it was coined as a posthumous compliment to John Mercer, a Broadoak (Lancashire) colourist, who, as the patent records show, was the first experimentalist to make a study of the action of cold concentrated caustic alkali on cotton cloth. He noticed, amongst other changes, the pronounced contraction and swelling of the fibres that occurred during attempts to filter concentrated caustic alkali solution through cotton cloth, but he did not observe that lustre was developed on the cloth if the normal contraction were prevented by mechanical force and the alkali-impregnated cotton washed while under tension. This observation, which led to the development of the modern mercerising process, was made by H. Lowe, England, and independently at a later date by Thomas and Prevost of Crefield, Germany. Unfortunately, the meaning of the term "mercerising" has been extended since Lowe's discovery to indicate almost any kind of treatment applied to cotton, etc., provided it involves the use of caustic soda solution of medium or high concentration. The mercerising process discussed in this article is confined solely to the modern practice of increasing the natural lustre of cotton by means of strong swelling agents, usually caustic alkali, with the aid of massively built impregnating and stretching appliances. Instead of preventing caustic-alkali impregnated cotton from contracting in the normal way, the cloth may be allowed to contract to its fullest extent, then stretched to near its original dimensions and the caustic soda removed by washing while it is in a stretched condition. Although the lustre developed in this way is not inferior to that produced by the more familiar method of working, *i.e.* by preventing too much contraction immediately following the treatment with caustic alkali, it has been shown that the force required to stretch a contracted cloth back to its original dimensions (approx.) is much greater than the force required to prevent initial contraction. Consequently, the best modern practice of mercerising cotton cloth is based on the latter principle.

Mercerising Practice.—Cotton cloth is mercerised either in the grey state, *i.e.* direct from the loom, or after semi- or full-bleaching. In either case, the cloth is singed (*cf.* BLEACHING, Vol II, 5*a*) prior to the first wet-treatment operation. Mercerising before bleaching appears to be practised to a greater extent than after bleaching, although a better lustre is obtained, excess caustic soda is removed more readily and higher speeds of treatment are attainable by adopting the latter procedure. Bleached cloth is prepared for mercerising, during the last stages of bleaching, by passing it continuously, in rope form, from the last washing machine *via* a scutching machine (opening out to full width), through a heavy water mangle; finally, it is dried by causing it to travel over a series of revolving steam-heated drying cylinders.

Grey cloth is often treated with a desizing agent, *e.g.* malt extract, after singeing, or after mercerising, *i.e.* immediately before bleaching, in order to remove, from the warp threads, starchy matter originally introduced in the form of sizing paste for the purpose of strengthening them during weaving. If desizing takes place before mercerising, the washing, after the latter operation, to remove excess caustic soda, need not be so drastic as is necessary when desizing takes place after mercerising. In fact, it is customary to leave a small amount of caustic soda in the cloth after mercerising, if desizing has already taken place, so that it serves partly as the alkali for the first lye-boil of the bleaching process; in this case, the mercerised grey cloth is passed direct to the lye-boiling kier after excess caustic alkali has been removed in the mercerising process. The waste caustic soda from the mercerised grey goods is not so pure, of course, as that from bleached goods; consumption of caustic soda in the best types of plant is about 20–25% on the weight of the cloth.

The main physical phenomena that occur during the initial treatment of the cotton with concentrated caustic alkali are lateral swelling of the individual cotton hairs and untwisting of their natural convolutions. These effects vary in intensity and completeness according to the length of time of treatment with, and concentration of, the caustic alkali; they are also influenced by the degree of twist in the yarn, and the amount of starch, etc., on the warp threads. The highest lustre is produced, however, when swelling and untwisting are allowed to proceed to a maximum, but in commercial practice, a compromise is essential in order to enable the process to be carried out continuously and economically; 7°Tw. caustic soda has no appreciable swelling action on bleached cotton; 15°Tw. caustic soda produces a distinct swelling effect, and swelling is at a maximum with about 45°Tw. caustic soda. Also, in the case of purified cotton, the action is complete in about 30 seconds when 60°Tw. caustic soda solution is used, whereas with grey cotton, a longer period is needed before the maximum changes occur. Consequently, in the design of plant for a continuous system of mercerising, the speed of the cloth is arranged to give a minimum action-period of 30 seconds, *i.e.* between the time of impregnation with caustic alkali and the first rinsing treatment.

Mercerising Plant for Cloth.—A typical modern cloth mercerising plant or range consists of (1) one or two impregnating mangles; (2) a hydraulic tension regulator for the warp threads; (3) a clip stenter with accessory apparatus, *i.e.* rinsing apparatus and compensating tension rollers between the end of the stenter and caustic alkali recuperator; (4 and 5) caustic soda recuperator and neutralising and rinsing boxes. The procedure briefly is as follows: The dry cloth, in open width, is drawn through cold caustic solution in (1) and squeezed between rollers under high pressure; this operation may be repeated while the cloth is travelling forward continuously. In high speed work, the cloth passes next over a series of hollow iron drums fixed close together; this operation allows time for the alkali to act and prevents shrinkage before the cloth passes through a second impregnating mangle and then *via* the expansion rollers of a warp-tension device (2), on to a stenter (3), where it is gripped powerfully at the selvedges by clips; after passing along the stenter for about 20 ft., the cloth is subjected to the first rinsing operation; next it is released automatically from the clips at the end of the stenter and then passes over compensating rollers into the recuperating box (4), from which it passes through dilute sulphuric acid and is finally rinsed thoroughly with water (5).

(1) *Impregnating or Padding Mangle.*—This consists of a box comprising two compartments for holding caustic soda solution; it is provided with a few guide rollers in each compartment for depressing and guiding the cloth through the alkali; also it is usually jacketed so that the temperature of the alkali can be kept constant. In the most efficient system of mercerising, two mangles, each having two compartments, are used, and the concentrations of the caustic soda liquors in the four compartments increase progressively from about 35° to 55°Tw. A tier of three bowls or rollers is placed immediately above each box; the projecting steel centres of these rollers are supported at both sides in bearings contained in exceptionally strong chucks; usually the bottom and top rollers of the tier are made of chilled iron, whilst the middle roller is covered with tough rubber. The rollers are positively geared to prevent slippage of the alkali impregnated cloth, and by means of pressure adjustments at both ends, the points of contact between the rubber periphery of the middle roller and the two other rollers when ready for operation, are brought into as perfect alignment as possible over the whole surfaces of the rollers. Although two mangles are used for rapid production, only one is required for cloth that is easily penetrated by the alkali.

(2) *Hydraulic Tension Regulator.*—This operates just before the cloth enters the stenter; its use prevents the weft from bowing and puckering. It consists of three guide rollers, two of which are fixed in a horizontal plane, whilst the middle roller operates hydraulically between the other two, so as to develop a constant hydraulic load over the whole width of the cloth and hold the warp threads at a predetermined tension.

(3) *Stentering Machine or Stenter.*—The essential features of this machine are two series of self-feeding clamps made of hard nickel grip plates and carried on endless chains running in races; a series of clamps is carried in a chain at each side of the machine; both series of clamps, as well as the travelling cloth, are in a horizontal plane, and are so constructed that a portion of each selvedge of the travelling cloth, as it enters the machine, is gripped automatically by a grip plate; as the cloth travels forward, more adjacent grip plates come into action, so that a long piece of cloth is held firmly in position in a pre-determined width while in a state of motion and thus is prevented from contracting; excess caustic soda is removed by spraying the top of the cloth with hot dilute caustic soda solution; the wash-liquor collects at each spraying point, and is directed by means of a doctor or scraping appliance to a point immediately over perforated suction boxes beneath the cloth, a vacuum pump being used to provide the suction. Rinsing is done on the counter current system and, when the alkali has been reduced to about 15°Tw., no further shrinkage of the cloth is likely to occur. The caustic alkali removed by rinsing is passed forward to a purification and concentration plant. The cloth is released automatically at the end of the stenter and passes through compensating rollers to regulate its speed of travel with that of the driven rollers in the alkali-recuperating box.

(4) *Alkali-Recuperating Box.*—This consists of several compartments containing guide rollers for the travelling cloth against which low pressure steam is blown; most of the residual caustic soda collects at the bottom of the box.

(5) *Neutralising and Rinsing Boxes.*—The cloth from (4) next passes between squeezing rollers into a tank containing 1½–3°Tw. sulphuric acid at 50°C.; it is then washed by jets of water while passing through another box, and after passing through a third box containing clean water, it is squeezed; if the cloth is in the grey state, it may then be desized and subsequently bleached, as previously outlined on p. 184*c*. If, however, the cloth has been partly bleached before mercerising, the souring and final washing operations may be omitted and bleaching completed in the usual manner.

Chainless Mercerising Machine.—This machine is provided with similar impregnating boxes, intermediate drums for preventing shrinkage in width and the same type of hydraulic tension regulator as those used on the chain machine; but the chains and clips on the latter are replaced by a series of curved expanders whereby in conjunction with the warp tensioning regulator, the cloth, as it passes continuously through the machine, is expanded to its full width before it enters the rinsing compartments. Six expanders serve to produce this effect; they are covered with rubber to enable the slippery alkali-impregnated cloth to be gripped more firmly than by metal surfaces. The cloth next passes over another series of expanders in a rinsing box which is divided into sections, the fresh hot rinsing water being caused to travel in the opposite direction to that of the cloth. Machines of this kind can be used for mercerising two pieces of certain types of cloth in juxtaposition in one passage (*v.* B.P. 210484, 295062).

Mercerising Union Fabrics of (A) *Cotton and Rayon*; (B) *Cotton and Cellulose Acetate Rayon.*

(A) Cloth composed of cotton and viscose rayon may be mercerised in a similar way to that adopted for cotton cloth; it is best, however, to wash out the alkali as quickly as possible with boiling water (*cf.* B.P. 295062). Cloths made from composite yarns of cotton and viscose rayon staple fibre (up to about 20% of the latter) can also be treated similarly. It is essential to remove excess alkali as quickly as possible in the initial rinsing operation and perhaps this is best done by a series of spray pipes through which nearly boiling water is sprayed on to the material.

(B) Mixture cloths containing cotton and cellulose acetate rayon fibres can also be mercerised in the same way as cotton cloths (*v.* B.P. 210484). The period of contact of the alkali with the cloth should be reduced to a minimum, consistent with the mercerisation of the cotton portion, whilst very thorough and quick washing with large volumes of cold water is essential, otherwise the cellulose acetate portion of the cloth is liable to become partly hydrolysed by the diluted alkali. Thus, a typical process of mercerising, dyeing and finishing cloths of this type involves the following operations—Singeing on both sides of cloth; desizing; rinsing; drying; mercerising; scouring in soap solution at 80–85°C. on jigs; rinsing; dyeing; rinsing; impregnating with a softening agent, *e.g.* highly sulphonated castor oil; stretching or stentering; drying; light calendering; and packing, etc., for delivery to customers.

Finishing Woven Cotton Fabrics.

The chief operations carried out in finishing cotton fabrics are—Stiffening, filling or weighting, drying, dampening, stretching, calendering, beetling, etc.

(1) STIFFENING.—The main object in this operation is to give the cloth a firmer handle. It is accomplished by impregnating the fabric with gelatinised starch or with gums, etc., with or without the addition of softening agents, *e.g.* glycerol, sulphated oils, etc., followed by drying. The degree of firmness attained is governed by the nature and consistency of the starch mixture used, and the amount absorbed and/or forced into the cloth by mechanical pressure and/or friction. Usually, the starch mixture is applied by means of a starch mangle. This type of machine is available in many different modifications, but similar principles are involved in nearly all types. In order to remove creases and impart slight tension, the dry cloth is drawn in full width over one or more tension rails direct into the stiffening mixture contained in a box (starch box) provided with a closed steam coil, waste outlet, etc., and situated immediately beneath 2 or 3 heavy bowls or rollers commonly arranged in a vertical plane. The box is fitted with one or more rollers for the cloth, which, on emerging from the paste, is then drawn over a rail or opener into the "nip" of the two lower rollers.

Thus, the starch paste, etc., is squeezed into the cloth and where a light stiffening is required, this operation is sufficient. For heavier effects, however, a three-bowl mangle is used, and in this case the cloth passes first between the lower nip and then between the upper nip, *i.e.* the points of contact between the upper and middle bowl or roller. The bowls are usually made of brass, cotton, sycamore, rubber, etc., and are arranged in suitable combinations according to the type of cloth to be treated and the finished effect required. Thus, a common combination consists of two cotton or sycamore bowls with a brass bowl between them, *i.e.* a three-bowl mangle. The middle bowl is positively driven so that all three bowls revolve at the same circumferential speed. An elastic uniform pressure at the nips of the bowls is secured by means of compound levers and weights fitted to strong side frames acting on the steel end cores of the bowls.

Friction Starch-Mangle.—This machine is used when fairly heavy fillings are used to fill up completely the meshes of the cloth and to secure a full, solid and stiff finished effect. It is a two-bowl mangle, the lower bowl being made of cotton and the upper one of brass. The lower bowl is partly immersed in the filling mixture contained in the starch box, and, as it revolves, it carries round to the nip a portion of the filling mixture. The speed of travel of the cloth is about the same as that of the brass bowl, but greater than that of the cotton bowl. After passing over tension rails and an opening bar, the cloth passes direct between the two bowls and, as the surface speed of the cotton bowl is slower than that of the brass bowl, a combined friction or rubbing effect with pressure develops between the cotton bowl and the cloth, whereby the interstices between warp and weft and the fibres themselves are filled up completely with the starch. The amount of friction set up can be varied at will by the use of change wheels.

Back-Filling Mangles.—Certain kinds of white cloth and also many calico prints are filled or stiffened on the back only. For this purpose, a back-filling mangle is used. The cloth is drawn over tension bars and a crease rail; its face is then brought into close contact with the underside of a large bowl; part of the latter revolves in a starch mixture contained in a starch box, so that the back of the cloth takes up the starch filling, the face being protected by close contact with the bowl; surplus starch is removed from the cloth, as it leaves the bowl, by means of a scraper or doctor, whilst another doctor scrapes the surface of the roller clean before it re-enters the starch mixture in the box. Another method of back starching or filling involves the following arrangement—A brass feeding roller revolving in the starch mixture feeds the latter to a brass starching roller which supplies the material to the underside of the travelling cloth. Adjustable side rollers are used to depress a given area of cloth on to the starch roller and a doctor removes surplus starch from the starch roller; the starch paste may be stirred by mechanical means.

Filling or Weighting.—When it is necessary to increase considerably the normal weight of a fabric, it is customary to impregnate the material with a glutinous mixture containing one or more so-called weighting agents, *e.g.* china clay, magnesium sulphate, etc. In certain cases, a thin filling consisting mainly of a strong solution of magnesium sulphate is used. Fillings of this kind are generally applied by means of a three-bowl starch mangle.

Drying.—The cloth is dried immediately after stiffening or filling; it is often carried out by passing the cloth over a series of steam-heated cylinders. In large scale work, so-called finishing ranges, each consisting of a starch mangle etc., and drying arrangement, are in use; the driving mechanism is designed to enable the cloth to pass through the starch mangle and over the drying cylinders at the same rate of speed. In some cases a short stenter (stretching apparatus) is placed between the starch or filling mangle and the drying machine, so that stretching immediately follows the stiffening, or filling operation. This arrangement is especially useful when printed goods exhibiting check or border designs are being finished, as well as in other cases where a straight weft and a definite finished fabric weight are required. Drying by means of hot air is essential in many cases. Usually, the cloth is drawn forward over guide rollers in a closed chamber, while a current of heated air is directed against it. Drying in conjunction with stretching, *i.e.* while the cloth is passing through a stenter, is also carried on with many woven structures. In this case, hot air is blown downwards and upwards through the travelling cloth. Finishing ranges comprising a starch mangle, a few steam-heated drying cylinders, a compensator mechanism to regulate the speed of the cloth between the cylinder drying machine and a stenter, are very largely used in the finishing of a wide variety of bleached, dyed and printed cloths, especially goods that do not require much stiffening. After being drawn through a finishing mixture contained in a starch box, the cloth is squeezed and then passed over a few steam-heated cylinders in order to raise the temperature of the cloth and start evaporation of the water present in the applied starchy, etc., finishing mixture. Next, the cloth is passed over a speed compensator apparatus direct to the stenter, where it is gripped at the selvedges and stretched to the required width while passing continuously forward to the exit end of the machine; during its passage through the stenter, hot air currents are directed on the under and upper sides of the cloth, whilst, at the same time, a to- and fro-movement can be given to the cloth (jigging) while it is held tightly in the stenter clips; this action imparts an elastic finish to the cloth. Also, a weft straightening appliance is attached now to most high grade modern stenters.

Conditioning, Dampening, Breaking.—An operation included under one of these terms usually takes place before subjecting the starched or filled and dried cloth to any treatment which involves the use of pressure or friction. Its object is to impart a mellow feel to cellulosic and silk fabrics. Some varieties of starched or filled cloths, however, do not require dampening before calendering, but, in such cases, it is advisable to allow the dried cloth to lie exposed to air before it is calendered. The two best-known types of machines used for conditioning cellulosic fabrics, work on the brush and spray systems, respectively. In the brush machine, a circular brush of bristles or copper spikes is caused to revolve at a high speed in contact with water in a trough. As a result, water is thrown upwards against two hinged lids which can be closed together in the centre. By adjusting the size of opening between the lids, it is possible to apply almost any degree of dampness to the cloth as it is drawn rapidly in a horizontal plane above the opening. In the spray machine, water under pressure is discharged from a special nozzle on to an inclined disc which atomises and directs it on to the underside of the travelling cloth.

Printed cloth is often conditioned slightly and stretched on a stenter provided with a weft-straightening motion. In this type of machine, dampening boxes, containing perforated steam pipes covered with gauze, supply the requisite moisture while the cloth is drawn over them; or it may be passed through a steaming box immediately before entering the stenter. The travelling cloth is dried by means of a series of steam-heated gilled pipes fitted underneath the stenter.

Stretching.—Most cloths shrink in width and increase in length during wet-processing operations and, in accordance with the merchants' instructions, the finisher is required to deliver different batches of cloth at definite widths which are generally less than the original widths of the woven cloth. It is invariably the practice in all the operations immediately following wet-processing to apply tension weft way at every opportunity before the final stretching operation is carried out. Two main methods of effecting the latter operation are in use, *viz.* stenter stretching and belt stretching. Stretching by means of a stenter is the most important method and has been almost universally adopted. It is carried out by stenters of the types already described on pp. 185*c*, and 187*a*. Belt stretching is conducted by means of a machine in which the two selvedges of the cloth are gripped tightly on the left and right, respectively, between the rims of two large pulleys and the belts running over them. The pulleys are placed at an angle so that the width between their rims at the entry end of the machine is less than that at the entry end of the machine, and this difference may be increased or reduced by a screw arrangement as required. Additional stretching rings are provided to enable the cloth to be stretched across the whole width.

CALENDERING.—This is practically the last main operation to which all classes of cellulosic and silk goods are subjected in finishing processes. Innumerable effects, which are governed largely, of course, by the amount and nature of the filling introduced at the starch mangle, padding box, etc., varying in handle from a soft mellow feel to a somewhat hard feel, *e.g.* buckram, and in lustre from a comparatively dull surface to one resembling polished glass, can be obtained by the correct choice of calenders. A calendering operation is somewhat similar in elementary principles to those underlying the use of the ordinary domestic iron. The simplest type of calender consists of bowls in vertical alignment, one of which (middle) is of highly polished and trued chilled iron and the other two of cotton. The steel centres and ends need to be exceptionally strong so as to enable them to withstand heavy shocks and fatigue while in use. The bowls are supported by their ends in bearings held in a strong cast-iron side frame; in some types, roller bearings are used. The bowls can be raised or lowered, and pressure is applied to the nips by means of compound levers and weights with regulating screws; or a " dead-set " pressure may be applied.

All calenders are provided with tension rails for entering the cloth and batching apparatus for winding the calendered cloth into a roll. When a high degree of lustre is required on certain cloths, at least one of the chilled iron bowls is provided with an arrangement whereby it can be heated internally by steam, or a compressed air and gas mixture may be used.

Friction calenders, light or heavy, working on the same principles as friction-starch-mangles, but of greatly increased strength (*cf.* p. 186*d*) are largely used for producing a glazed face-finish on grey finished cloths, dyed and printed goods, bookbinding and tracing cloths, etc. In order to prevent the cloth from slipping while passing between the nips, the metal bowls are geared together.

Multiple bowl ordinary calenders, provided (*a*) with at least one metal bowl, which can be heated by combustion of a mixture of compressed air and gas, or (*b*) with two or more bowls arranged for heating with steam, are used in various sections of the textile and paper finishing industries. The bowls are made of chilled iron, cast iron, steel, brass, cotton, linen, or woollen paper, and are used in various combinations to suit the particular type of fabric which is to be calendered.

So-called universal calenders also are in use; they are designed to be used for various purposes, *e.g.* cold calendering, swissing, chasing, etc., but for heavy pressure work it is best to use special types. The chief technical terms used in calendering, etc., and their definitions are:

Swissing.—A method of imparting a soft and mellow feel to cellulosic fabrics, *e.g.* many kinds of printed cloths, as well as white, dyed and coloured woven goods. An ordinary three-bowl calender with one chilled iron bowl working between two cotton bowls is commonly used. If desired, the iron bowl can be heated by steam.

Chasing.—The production of a thready, lustrous, imitation beetle-finished effect on cotton, etc., cloth. The cloth, in multiple folds, is passed continuously through a calender with five or more bowls, *e.g.* two of chilled iron (one of which can be heated) and three of cotton.

Chesting.—A method of imparting a thready and water-marked or moiré finished effect. It is produced by passing the cloth, from bottom to top, between a series of calender bowls, and then batching, *i.e.* winding it into a large roll of calendered single-ply cloth on the top bowl and causing the roll of cloth to revolve for some time under heavy pressure. This operation is often known as rolling or mangling.

Schreinering.—A process of embossing the face of the cotton cloth with a series of continuous closely packed lines so as to produce a silky effect. The cloth, which has been conditioned so as to contain a little more than its normal moisture content, is passed between two bowls of a Schreiner calender. The top or driving bowl is made of special steel bored centrally for heating with steam or gas and air; after polishing to a high degree, it is engraved with fine fairly deep lines or cuts usually running very close together round the bowl. The number, and the angles of the lines, in relation to the axis of the bowl, vary according to the type of fabric to be schreinered and the twist of the warp yarn. In most cases, the angle of the engraving is nearly the same as that of the twist of the yarn so that the natural reflecting surfaces help to increase the lustre produced by the embossed lines. A bowl for schreinering ordinary twill, sateen, etc., fabrics, usually is engraved with about 200–300 lines per in., but for the production of the highest degree of lustre, a bowl having 500 lines per in. may be used. The lower bowl is much larger in diameter than the steel bowl; it is usually made of hard pressed cotton or woollen paper. A so-called spun-glass finished effect can be obtained by setting up friction while the cloth is under great pressure. In this arrangement, the steel bowl is engraved with concentric lines at right angles to its axis; it impresses the lines on the cloth parallel to the warp threads and the new surface thus obtained is polished by the friction set up between the bowls; friction wheels are available to impart the requisite amount of friction.

BEETLING.—A method of imparting a smooth and thready effect to many kinds of linen and cotton cloths. The operation tends also to close up the interstices between the warp and weft threads. Several webs or pieces of conditioned cloth are wound on to a roller and the roll then caused to revolve slowly while a series of heavy wooden rounded-end " fallers " drop one after another on to the cloth and are immediately lifted by a cam attached to a revolving shaft; the fall and lift movements go on continually while the rolls are caused to move laterally about 3 in. during the operation. Metal hammers, attached to a specially designed machine, enable the process to be completed more quickly than with the wooden hammer type of machine, owing to the rapidity with which elastic blows from the hammers fall on the cloth. The finished effect, however, is not considered to be as attractive as that produced by wooden fallers.

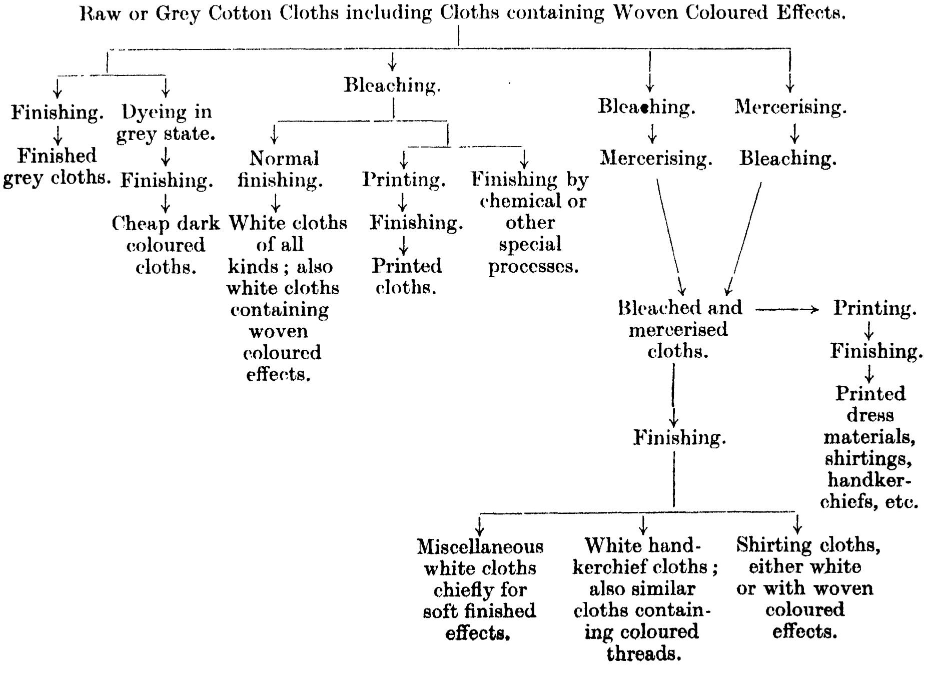
Embossing.—Imprinting a design cut in a steel bowl on to the surface of cloth. This operation is analogous to schreinering, but the lines on the steel bowl are coarsely engraved and they number only about 150–250 per in. Bowls with lines cut at an angle of about 45° are commonly used for embossing bookbinding cloth. In contrast, appropriate lines may be cut at the usual angles on the steel bowls and then portions of the lines cut away and a figure engraved *intaglio.* These bowls give a less lustrous effect at the figured portions; again, only the figured portions may be engraved with fine lines, thus giving lustred figure effects on a smooth ground.

Finishing Materials.

A large choice of compounds suitable for use as stiffening, filling, softening, etc., agents for cellulosic cloths is available. They may be classified as (1) stiffening and binding agents; (2) filling and weighting materials; (3) softening and emulsifying agents; and (4) miscellaneous substances. Some of the materials in one group may also act as members of another group. Thus, although glycerol is a softening agent, it also acts, by virtue of its hygroscopic nature, as a weighting agent. The chief materials in each of the groups are: (1) Potato, maize, wheat and rice starches; also sago and wheaten flours. (2) China clay, mineral white (calcium sulphate), French chalk or talc and a related American product known as talc clay (hydrated magnesium silicate), magnesium sulphate, etc. (3) Soaps, especially castor oil soap, Turkey red oils of various grades of sulphation and sulphonation, sulphated higher aliphatic alcohols, various proprietary compounds containing long-chain aliphatic groups, *e.g.* synthetic higher fatty acid esters of glycerol, glycol derivatives, etc. (4) Glycerol and glycerol substitutes and zinc and magnesium chlorides (hygroscopic agents); salicylic acid derivatives, *e.g.* "*Shirlan*" (antiseptics); natural and synthetic waxes (glazing and softening agents); various water-, fire- and moth-proofing substances; wetting-out and anti-crease agents, etc.; ultramarine and various blue and violet dyes (tinting agents); cellulose derivatives including cellulose nitrate lacquers; also many other substances.

Preparation of Finishing Pastes, etc.—Ordinary finishing pastes are made in round or square tanks provided with mechanical agitators and means for heating the pastes by direct or indirect steam. Starches are first mixed uniformily with cold water and then boiled well during agitation; flour is first mixed to a smooth paste with cold water, then thinned by the addition of more water and boiled; the other ingredients are added as required. The concentrations of starch, etc., used, vary con-considerably according to the nature of the cloth to be stiffened and the kind of finished effect required. Starch pastes should be entirely free from lumps before they are placed in the box of the starch mangle.

Main Divisions of Cotton Cloth Finishing.—A rough classification of the chief divisions into which the finishing of cotton cloths may be grouped is given in the following diagram—


Raw or Grey Cotton Cloths including Cloths containing Woven Coloured Effects.
Finishing.
Finished grey cloths.
Dyeing in grey state.
Finishing.
Cheap dark coloured cloths.
Bleaching.
Normal finishing.
White cloths of all kinds; also white cloths containing woven coloured effects.
Printing.
Finishing.
Printed cloths.
Finishing by chemical or other special processes.
Bleaching.
Mercerising.
Mercerising.
Bleaching.
Bleached and mercerised cloths.
Printing.
Finishing.
Printed dress materials, shirtings, handkerchiefs, etc.
Finishing.
Miscellaneous white cloths chiefly for soft finished effects.
White handkerchief cloths; also similar cloths containing coloured threads.
Shirting cloths, either white or with woven coloured effects.

Examples of the technique followed in producing various kinds of finished effects are as follows:

Heavy Grey Sheeting.—The cloth is stiffened on a friction starch-mangle with a paste containing about 12% white dextrin, 1·5% maize starch, previously boiled together, with addition of about ⅛% glycerol, ⅛% Turkey Red oil. Finally it is dried and passed through one calender.

Cotton Cloth Dyed in the Grey State.—The cloth is first calendered and then impregnated with a solution made by dissolving ½ cwt. Glauber's salt in 3 gallons water containing 3 quarts each 48°Tw. magnesium chloride and 100°Tw. zinc chloride and then adding sufficient magnesium sulphate to give, on cooling, a 55°Tw. solution. Drying and calendering complete the process.

Grey Cloths with Coloured Checks or Borders.—The cloth is impregnated, on the starch mangle, with magnesium sulphate, etc., solution or with a starch paste which may or may not contain magnesium sulphate. It is then dried on steam-heated cylinders, stretched on a short stenter with a weft straightening attachment and finally calendered as desired.

Bleached Cotton Cloths.—(1) *Soft Handkerchief Finish.*—The bleached cotton is water-mangled, dried, conditioned, stretched (belt stretching machine) and swiss calendered on both sides by passing through a multiple bowl calender.

(2) *Bottle Finish.*—The bleached cloth is water-mangled (with ultramarine blue in the box) dried, dampened, stretched, calendered (chased) and beetled for 15 minutes each end.

(3) *Stiff Finished Effects.*—The degree of stiffness is varied according to requirements by using pastes made from mixtures of starches and dextrin in different proportions; in a few cases, small amounts of mineral weighting agents are used; Turkey Red oil or other suitable agents are usually added to the pastes to soften the harsh effect imparted by the starch, etc., and ultramarine blue is added to counteract the slightly yellowish tint of the fabrics and the resultant starch films produced during drying of the filled material. The general procedure in nearly all cases is as follows: Water-mangling, drying, filling or starching; stretching, drying, cooling, dampening and calendering. By varying the nature and concentration of the filling pastes, and using suitable cold or hot calenders to give gloss, compactness, friction effects, etc., almost any kind of finished effect can be obtained.

Finished Effects on Dyed and Printed Cloths

The p_H of a finishing paste may influence the tone of the colour of the dyed cloth. Consequently, it is best to use neutral mixtures or, in some cases, *e.g.* sulphur dyeings, slightly alkaline pastes. Mercerised cloths, *e.g.* shirting and handkerchief cloths, etc., are rarely filled with starchy substances which yield harsh opaque films on drying, because such cloths need to exhibit lustre and possess a soft handle. This statement applies to all cloths which should possess a soft mellow handle. When a dyed cloth is required to possess a stiff handle, the filling itself is often dyed, *e.g.* it is mixed with an appropriate dye solution. Thus, some black-dyed cloths of this kind are filled with a starch-dextrin paste which has been coloured with a direct cotton black dye. The operations and their sequence are similar to those described under the finishing of bleached cloth. When a special finished effect, *e.g.* an embossed effect, is required, it is common practice first to pass the cloth through the usual operations, in order to help to close up the spaces between warp and weft and flatten the surface threads. The special effect is then obtained by a final mechanical treatment designed for the purpose, *e.g.* embossing.

Several types of printed cotton cloths are back-filled. The usual procedure is as follows—The dry cloth is back-filled with a starch paste-china clay mixture containing a little softening agent and ultramarine blue. It is then dried, cooled, conditioned, stretched if necessary, and finally passed through an ordinary cold swissing calender.

Shirting Cloths containing Woven Coloured Stripes.—The dyes used for the coloured yarns in good quality shirting cloths are generally of the vat and azoic classes, so that such cloths are able to withstand scouring with alkali and bleaching with hypochlorites without the dyes bleeding on to adjacent parts of the fabrics; this defect may occur, however, if the goods, while wet, are allowed to lie about in heaps. A typical complete wet-processing and finishing procedure is as follows: Singeing, desizing, rinsing, lye-boiling in open-kiers (about 100 lb. soda ash and 20 lb. soap for 3–4 tons of cloth), bleaching (1°Tw. bleaching powder solution at 80°F. for 1 hour), rinsing, scutching, drying, impregnating with a softening agent, stentering, chase-calendering, pre-shrinking, *e.g.* Sanforising or Rigmelising (*see* p. 193), and making up for sale.

"Permanent" Finished Effects on Cotton and Linen.—Cotton and some other cellulosic fibres may be caused to exhibit distinctive finished effects either by (1) direct chemical action and/or solvent action on the fibre; (2) by the introduction of chemical compounds, usually *via* solutions or emulsions into and/or on the fibres, followed by removal of the dispersing medium; in the latter case, a subsequent heat treatment may be used to induce a final chemical change between suitable compounds deposited or precipitated on the fibres; and (3) by mechanical means, *e.g.* the Sanforised and Rigmel finishes.

Effects produced by any of the methods used in the three classes are either permanent or semi-permanent to washing, etc., during a normal period of use. Many permanent finished effects are obtained in cases where the main object is to render fabrics impervious to water (*see* "Waterproofing," p. 197*c*).

(1) PERMANENT EFFECTS PRODUCED BY DIRECT CHEMICAL AND/OR SOLVENT ACTION ON CELLULOSE.

Translucent, Parchment, and Wool-Like Effects.—A short treatment of cotton cloth with cold

77°–110°Tw. sulphuric acid, followed by washing yields a semi-translucent slightly stiff fabric; both stiffness and translucency, *i.e.* parchmentisation effects, increase considerably if acid of higher concentration is used, but at the same time, the action of the acid is more difficult to control. As a result, the commercial application of the process is mainly confined to the use of acid of medium concentrations for the production of so-called Organdie or Heberlein effects. Fabrics which have been treated in this way, absorb dye with the same avidity as mercerised cotton; the best results are obtained on scoured and bleached material. Sulphuric acid below 90°Tw. has only a slight parchmentising effect on cotton, although the treated material has an increased affinity for dyes. Alternate treatments of cotton with cold 108°Tw. sulphuric acid (followed by washing and removal of excess water), and with 50°Tw. caustic soda solution, cause it to exhibit a wool-like handle and appearance. Nitric acid or mixtures of this with sulphuric acid, concentrated phosphoric acid, 142°Tw. zinc chloride solution, cuprammonia, substituted quaternary ammonium bases, etc., may be used instead of sulphuric acid. The treatment with mineral acids is best carried out at about 0°C., but higher temperatures may be used, provided that substances which slow down the swelling power and normal hydrolytic action of mineral acids, etc., on cotton cellulose, are added to the impregnating baths; such substances as glycerol, pyridine, alcohol, etc., have been suggested for this purpose; some of them tend to soften the parchmentising effect produced by the action of acids alone. Other agents used for the same purpose are formaldehyde, ammonium sulphate, etc. Mixtures of formaldehyde and sulphuric acid may be applied to cotton in order to produce a crêpe effect, whilst excellent imitation damask weave effects can be obtained by printing cloth with thickened mixtures of these compounds. That there are innumerable ways in which a combination of parchmentising and mercerising operations can be utilised to give different finished effects and the wide choice of compounds available for the purpose, will be obvious, but with the reservation that when cotton has been swollen by any process it is far more susceptible to degradation by subsequent treatment, especially those that tend to induce hydrolysis. A process termed " Philanising " for imparting to cotton the characteristic features of wool was patented a few years ago. It consisted in the treatment of cotton cloth direct from the loom, *i.e.* cloth containing natural and artificial impurities, with cold (>65%) nitric acid, followed by washing, and bleaching with sodium peroxide. In general, when the swelling of cotton takes place without tension, wool-like effects are to be expected, but if the fibre is swollen and subjected to tension, a wide range of effects, varying from those of the slightly stiff semi-translucent types to comparatively soft, smooth, lustrous semi-transparent types, is obtainable.

Resist Effects against Substantive Dyes.—The most satisfactory method of modifying cotton so that it will not dye with substantive (direct) dyes, is to convert it into cellulose monoacetate which, apart from its sensitivity to alkali, may be regarded as a permanent finish. This effect, originally introduced by the Sandoz Chemical Co., Ltd., is usually produced in the form of treated ordinary or mercerised yarns; if desired, the yarns may be dyed before conversion into cellulose monoacetate, suitable dyes being used for the purpose, and subsequently woven along with ordinary yarns which are then dyed in contrasting colours, thus yielding multicoloured fabrics. The resist yarns are known as " *Kotopa* " and " *Krestol* " yarns.

Permanent Finished Effects produced by the Action of Solvents.—One of the earliest methods of producing a surface modification of cotton fabrics was dependent on the controlled solvent action of cuprammonium, followed by treatment with acid or other suitable coagulant, washing, calendering and drying. Fabrics treated in this way are often known as Willesden fabrics. They are somewhat stiff, pale green in colour owing to the presence of cupric cellulose complexes, and fairly resistant to water and to attack by lower organisms. A simple modern modification of the process involves the padding of the cloth with a dispersion of cellulose in cuprammonium, followed by drying to precipitate the dispersed phase; if desired, trimethylbenzylammonium hydroxide (" *Triton B* ") may be used in place of cuprammonium.

(2) " Permanent " Finished Effects Produced by Synthetic Resins

The use of a synthetic resin in finishing cotton cloth was first practised on a large scale by Tootall Broadhurst Lee Co. Ltd., of Manchester (*see also* p. 198*d*). This firm discovered that the normal creasing property of cotton was reduced considerably by inpregnating cloth with a small percentage of urea and formaldehyde in presence of a catalyst and then inducing a medium degree of polymerisation of the simple initial condensate by heating the cloth momentarily at a high temperature, *e.g.* about 150°C. This practice results in the formation of an insoluble resinous polymer throughout the fibre structure; the degree of polymerisation of the resin apparently governs the nature of the physical effects exhibited by the treated fabric. The best results are said to be obtained by using an impregnating solution containing an organic acid catalyst, *e.g.* tartaric acid, and sufficient ethanolamine to render the liquid neutral. After the perfectly dry cloth has been impregnated, it is dried and the final condensation of the resin effected as already indicated. The treated fabric is more resilient, wool-like and less creasable than the original fabric. The interest created by the publication of the patent specifications, and the exploitation of the process for the production mainly of crease-resistant finished effects by the Tootal Broadhurst Lee Co. Ltd. process have resulted in the granting of a large number of patents for new methods of finishing textiles with synthetic resins; for example, the more highly polymerised urea-formaldehyde resins are used as surface coatings on various fabrics and for producing anti-slip finished effects on rayon cloths. In general, the use of suitable synthetic resins, formed *in situ* on cloth, results, after calendering, embossing, etc., in the development of finished effects of good resistance to washing. Acid dyes can be applied to cotton and rendered fast to washing by similar means, *i.e.* dyes which dye only the resin can be used and the resin treatment may take place before or after dyeing and/or printing. Again, pattern effects may be produced by printing on the cloth a resist, *e.g.* citric acid, which prevents the formation of the resin polymer at the printed parts. Further, more tenacious yarns and fabrics are produced and a permanent weighting of up to 20% may be incorporated. Other directions in which synthetic resins are being used in the textile industry include the manufacture of multi-ply fabrics for collars, etc., which can be washed easily. Also, the use of staple fibre (spun rayon) will probably expand more rapidly as a result of the new technique of producing permanent finished effects on the woven cloth with synthetic resins. It has been found, for example, that ordinary spun rayon fabrics, after ordinary shrinkage, shrink further on washing, but when finished with a suitable synthetic resin they are unaffected on washing. Apart from the practice of forming the resin within the fibre substance, it is possible to produce clear continuous resinous films on the surface of the cloth. The general finished effects produced by the formation of synthetic resins on, and in, textiles, are brighter, clearer, more or less permanent and faster to washing than ordinary effects produced by long established methods. In addition to the urea-formaldehyde resins, it has been demonstrated during the past few years that the complex compounds, formed by polymerisation and condensation of methacrylic esters: glycerol-phthalic acid, vinyl chloride-vinyl acetate, melamine-formaldehyde, quaternary ammonium-formaldehyde-higher fatty acid complexes, etc., are valuable agents for the production of permanent and other finished effects on cotton and other fibrous materials. The resinous methacrylic ester polymers, for example, are formed at comparatively low temperatures and are of especial interest, therefore, in the finishing of silk, wool, casein fibres, cellulose acetate rayon, etc. A considerable number of commercial materials for producing resins of different degrees of polymerisation is now available, and the "permanent" finished effects on textiles obtainable with their aid vary to such an extent that nearly all the requirements of the public as regards appearance, durability, handle, fastness of dyeings to washing, etc., can be obtained with comparative ease. In addition, the treatment with synthetic resins of yarns and fabric intended for the manufacture of hose pipes and other articles which must be resistent to petrol, oils, etc., has already met with a certain amount of success. Some of the commercial products are soluble in water; some are sent out as aqueous emulsions, whilst others are soluble only in organic solvents, *e.g.* carbon tetrachloride. ("Permanent" finished effects of the water-repellant type are described under "Waterproofing," p. 197.)

"PERMANENT" FINISHED EFFECTS PRODUCED WITH CELLULOSE ETHERS.—Various commercial brands of cellulose ethers and hydroxyethers sold under proprietary names have been advocated for use in different branches of the textile finishing industry for the past few years. The most important of these products are the hydroxyethoxy-derivatives of cellulose. They are usually classified as alkali- and water-soluble cellulose ethers, corresponding with products containing medium and comparatively high hydroxyalkoxy-contents. Methylcelluloses having somewhat similar properties appear to be more suitable for use as thickening agents for special styles in calico printing than as finishing materials, although they have been in commerce for a much longer period than the hydroxyethoxy-derivatives. The caustic alkali-soluble type of the latter is the most suitable product for use on cellulosic cloths in the development of finished effects reasonably fast to washing, wear, etc. It dissolves in 5–10% caustic soda solution at low temperatures, *e.g.* 5°C., to give fairly clear working solutions of about 2–7% concentration; higher concentrations tend to form gels. The clear solutions are stable at room temperature, but are likely to coagulate at about 60°C. Coagulation also takes place readily in presence of acids, salts and concentrated caustic soda solution. The cellulose ethers are remarkably stable when compared with cellulose esters. Consequently, they may be applied to cotton cloth either before, during or after the normal bleaching process.

According to Craik and Davis (J. Soc. Dyers and Col., 1939, **55**, 597), the product obtained by etherifying alkali cellulose with one molecule etherifying agent, *e.g.* ethylene oxide, per four molecules, $C_6H_{10}O_5$, is soluble in 5–10% caustic soda solution at ordinary temperature and is the most satisfactory of the cellulose ethers for use in producing permanent finished effects on cotton.

Craik and Davis (*l.c.*) give the following list of uses of this type of cellulose ether—Imparting linen-like finished effects to cotton; stiffening cotton, jute, rayon or spun rayon staple fibre; holding fillers or pigments in suspension up to a maximum of three parts filler to one part cellulose ether; doubling cloths; preparation of bookcloth, window hollands, photographic cloth and pigmented fabrics, etc.

Three methods of application of cellulose ethers are in use, viz. (*a*) a dispersion of about 3–5% cellulose ether in caustic soda solution is used alone for inparting linen-like effects to cotton cloth; (*b*) a cellulose ether is used as a medium for enabling heavy fillings, *e.g.* china clay, talc, etc., to be applied to low grades of cloth; such filling should not dust out when the filled cloth is torn or rubbed, and the new products are far superior to starch for producing fairly satisfactory laundry-resistant effects; (*c*) cellulose ether dispersions, with or without filling agent, containing soap or foam-producing material are beaten into a foam and applied to cloth by the usual means whereby the ether, on immediate subsequent precipitation by means of acid or salt solutions, assumes an open or cellular form; in this method, high concentrations of the ethers may be used without making the treated cloth too stiff. In most methods, the dispersion is padded on to the cloth; in some cases, back-filling is employed. Subsequent precipitation of the ether on the cloth is achieved by means of dilute acid; or the treated cloth may be dried carefully (foam method excepted) and then rinsed well in warm water to remove caustic soda. The cloth is then dried and/or passed through the requisite finishing machines, according to the final effects desired. Even grey cloth, immediately after singeing, may be impregnated with cellulose-ether dispersions and, after coagulation, *e.g.* by treatment with acid, the cloth may be passed in rope form through the normal bleaching process without greatly affecting the permanency of the cellulose-ether effect.

Production of Permanent Finished Effects by Formation of Cellulose Ethers in situ on Cotton Cloth.—According to B.P. 439880, 475906, 481191, and 482942, novel permanent finished effects, especially varying degrees of transparency and stiffness, can be obtained *in situ* on cotton cloth by the action of etherifying agents, *e.g.* ethylene oxide. The treated cloth can then be subjected to further finishing according to requirements. Various modes of etherifying the cotton cloth have been described by Lawrie, Reynolds and Ward (J. Soc. Dyers and Col. 1939, **56**, 6). Thus, cloth is impregnated with 1–2 times its weight of 9·5% caustic soda solution and brought into contact with a solution of ethylene oxide in (*a*) carbon tetrachloride or (*b*) brine; or (*c*) a solution of ethylene oxide in caustic soda may be used for the initial impregnation; or (*d*) gaseous ethylene oxide may be allowed to act on the alkali-treated cloth. Subsequent operations include recovery of solvent (if used), neutralisation of caustic soda, bleaching with weak calcium hypochlorite solution, rinsing and drying, the final dry-finishing operations being determined according to the nature of the final effect required, *e.g.* organdie-, linen-, parchment-like effects, etc. The process can also be used in printing for obtaining window pane, damask, figured velveteen, and lace effects.

(3) PERMANENT FINISHED EFFECTS PRODUCED BY MECHANICAL ACTION.

The Sanforising and Rigmel Processes.—In addition to the foregoing methods of producing permanent finishes by chemical means, two well-known methods of permanently positioning the threads of warp and weft in the woven structure are carried out entirely by mechanical means. The finished effects are known as Sanforised (B.P. 401617) and Rigmel finishes (B.P. 400950). The main object of these methods is to treat cotton cloths in such a manner that shrinkage, during laundering, of garments made from the finished cloth does not occur. Most cellulosic fabrics shrink in width and increase in length during scouring, bleaching, dyeing and other wet-processing operations owing mainly to (*a*) the release of torsional energy, (*b*) swelling of the fibres, and (*c*) to the pulling force commonly exerted lengthways. In the final finishing operations, therefore, it is often necessary to stretch the fabrics weft-way to the finished width required by the merchant. This operation produces a temporary set of the warp and weft threads and, as soon as the fabric is wetted out in water or soap solution, the yarns swell and twist until the unequal strains induced by finishing operations are relieved and the fibres have adjusted themselves. The inevitable result, therefore, is that shrinkage in area occurs. If the cloths have not been stretched weft-way mechanically, the shrinkage, of course, is mainly lengthways.

Sanforising.—Portions of the ordinary finished cloth are first passed through a severe laundering treatment and dried in order to determine the maximum shrinkage; the cloth is then marked accurately in order to check its length- and width-shrinkage during the process as calculated from the results of the laundering test. In actual Sanforising, the cloth is guided by electrical devices to rubber-grip and speed-control rolls in the Sanforising machine; these rolls are connected with variable speed gearing and shafts to the exit control cylinder, and by altering this gearing in accordance with the pre-determined shrinkage figures, it is possible to shrink the cloth mechanically and continuously to the requisite degree. The threads in the woven fabric are forced into closer contact by causing the cloth to adhere by pressure to the stretched surface of a belt in the Sanforising machine, and then causing contraction of the belt surface and the cloth in contact with it, according to the exact amount originally indicated by measurement of laundering-shrinkage. Finally, the contracted or shrunken cloth passes, in this state, over a heated exit cylinder where it is set by heat and pressure. As a result, the finished material emerges from the machine, fully shrunk in length and width, and exhibiting a smooth and satisfactory trade finish.

The Rigmel Process.—Two rollers, covered, for example, with rubber of 75–80° and 95–100° hardness, respectively, as measured on the Durometer, are pressed heavily together and caused to rotate at different speeds in opposite directions so as to cause distortion of the periphery of the soft roller. The pressure may be varied in degree as well as in direction. When a fabric is passed between the rollers, it shrinks longitudinally if the hard roller rotates more quickly than the soft roller. Conversely, an elongation of the fabric occurs if the peripheral speed of the soft roller is greater. The shrinkage is caused by the distorted resilient surface of the soft roller springing back or acting as a brake on the fabric in its passage from between the rollers, *i.e.* immediately it has passed the point of maximum pressure. Thus, the weft threads are forced into closer proximity to one another than is possible by any other process. The degree of shrinkage may be adjusted and pre-determined for any given fabric provided the soft roller is of sufficient thickness.

WATERPROOFING AND SHOWERPROOFING.

Two distinct systems of rendering textile fabrics resistant to penetration by water have long been in use. In one system, applicable mainly to cellulosic fabrics, etc., the material is coated on the surface with a homogeneous, continuous layer of various substances, *e.g.* rubber, or impregnated throughout its mass with oils and waxes, synthetic resins, etc., which, on subsequent treatment, yield fabrics that are impervious to water and air. In both these methods, the treated material invariably increases in weight, *i.e.* it is weighted as well as waterproofed and its physical properties are often altered to such an extent that it is unsuitable for use in the manufacture of wearing apparel. In the second system, the threads of the fabrics are caused to repel water, but the air spaces are not closed and the natural handle and other physical properties are either improved or only slightly affected. This system is often termed shower- or rain-proofing and may be applied either to cellulose or protein fibres. The treated goods are eminently adapted for the manufacture of wearing apparel. Showerproof or water-repellant fabrics offer considerable resistance to the passage of water owing to the absence of active chemical groups in the waterproof film and the low surface tension of the latter against air. As a result, any water falling upon the surface of the fabric is prevented from forming a continuous film, *i.e.* it tends to collect in the form of globules and, consequently, does not easily pass through the air spaces adjacent to warp and weft threads.

WATERPROOFING.

(A) USE OF RUBBER.—A considerable number of different types of cellulosic and other fabrics are waterproofed by coating them on one or both sides with rubber. Ordinary fabrics used for the manufacture of raincoats may be of cotton, wool, union cloth, silk or rayon. In the best-known method of applying rubber as a waterproofing material, a thin coating of rubber " dough " is spread uniformly, by means of a spreading machine, on to one side of the travelling fabric ; the thickness of the coating is determined by the use of a gauge which consists essentially of a steel knife or doctor. The dough or paste is made by thoroughly mixing sheet rubber, rubber substitute, sulphur and mineral filling agents, in powerful masticating or milling machines, and converting the mass into sheets which are finally mixed with solvent naphtha until a smooth paste of about the same consistency as bakers' dough is obtained. Several thin coatings of dough may be applied to a fabric. The first coating is the adhesive coat and fills up the pores of the cloth; the intermediate coating or coatings supply body, and the final coating is termed the " surface " ; the latter may be coloured as required, pigments fast to vulcanising being used. The fabrics are then vulcanised cold with a solution of sulphur chloride in carbon disulphide. In double-texture proofing, the " surface " coating applied to one side of a piece of cloth is a special composition termed varnish, which enables a second cloth to be cemented to it by passing them together between suitable rollers. In this kind of proofing, *e.g.* balloon casings, the treated fabric is usually subjected to a hot vulcanising operation, *e.g.* at 100–130°C., and the rubber dough used is made from best hard cure Para rubber without inorganic fillings, as these unfavourably affect the elasticity and durability of the rubber content. The total weight of the coatings applied to balloon cloth (usually consisting of closely woven fine Egyptian cotton yarn) is about 12 g. per sq. metre. Single texture coatings are usually vulcanised by drawing the cloth, under tension, round a 4 in. mahogany roller immersed in a vulcanising solution of 1 part S_2Cl_2 of not more than 51% chlorine and 50 parts carbon disulphide, followed by drying on a steam-heated cylinder. The whole of this process is carried out in an enclosed chamber; next, a current of hot air is blown against the travelling cloth which then passes through a chamber containing ammonia vapour; at one stage in the process, it is brushed with farina or other suitable dusting material.

In the steam-vulcanisation process, the coated materials are heated with steam under pressure at about 220–295°F. Under these conditions the rubber is completely vulcanised in a comparatively short time, especially if a suitable accelerator has been added to the dough. Material which is to be proofed with rubber should be free from traces of copper (not $>0{\cdot}02\%$), and manganese and the ether extract should not exceed about 1–2%. The outer layer of balloon fabric is generally dyed a yellowish-red shade with vat dyes before it is coated with rubber in order to act as a partial protection against the degrading influence of light.

(B) USE OF LATEX.—Although a dispersion of natural rubber in water stabilised with ammonia has now been available for many years, its use as a waterproofing agent for textile fabrics does not appear to have made much progress owing mainly to its poor penetrating properties and lack of adhesiveness. Further, unlike a coating of rubber dough, the rubber particles in latex do not become semi-fluid during vulcanising. As a result, surfaces that have been coated with latex are not smooth and the finished effects are often unsatisfactory. Various means of overcoming these defects have been proposed, but, in general, the methods are more costly and do not yield any better results, apart, perhaps, from a slightly improved quality, compared with effects produced by the rubber dough process. On the other hand, the low capital cost of the plant for applying latex, compared with that for the rubber dough process, should be an important factor in the exploration of possible uses of latex in finishing textiles. Latex films or coatings are usually vulcanised or cured in air, or water at <100°C. In this process, so-called ultra-accelerators are often used and, as milling is unnecessary, the defect of scorching does not occur. Water-soluble ultra-accelerators, *e.g.* the carbon disulphide reaction products of dimethylamine, piperidine and also the suitable alkali metal xanthates are to be preferred when curing takes place in hot water. Apart from its use for the production of a waterproof finish, latex, either alone or in conjunction with other film-forming substances, is finding many novel applications in the textile industries, but as many of them are in the initial stages of development, it is not possible at present to form definite opinions regarding their utility or their influence in long-established finishing practice.

(C) USE OF OILS, SYNTHETIC RESINS, CELLULOSE NITRATE, ETC.—In addition to rubber proofing, other methods of finishing fabrics in such a way as to render them impervious both to water and air have been in use for several decades. Further, the treated fabrics may be translucent, *e.g.* oiled cloth, or opaque, *e.g.* oilskins and American cloth or oil cloth, and in the case of the latter may exhibit coloured designs produced by printing and/or embossing.

Waterproof covering materials, built up in special ways on woven cotton cloth or other suitable base, have been made for many decades. In most cases they are intended to have high resistance to wear, whilst some of them are designed to imitate more expensive covering materials. The waterproof effect shown by such coverings is usually only one of several characteristic physical properties which are developed in the finishing processes.

American Oilcloth and Related Covering Fabrics.—The well-known white or pale-coloured, opaque, glossy cloth commonly termed oilcloth, and used for covering tables, etc., is made by applying coatings of a filling, *e.g.* a paste made by grinding china clay or lithopone in thickened linseed oil, to one side of a cotton fabric free from motes, fluff, etc., and allowing the treated fabric to dry at a medium temperature between each coating. The better qualities of cloth are "rubbed down" mechanically between each coating, dusted with French chalk and calendered. If the coated cloth is to be printed with a coloured design the last coating, which may contain a natural or synthetic resin, usually is flattened down level by means of a mechanical sander or polisher. Finally, whether the cloth has been printed or not, it is given a protective coating with a special varnish and allowed to dry. Since this last film or coating, formed on the cloth, largely determines the resistance of the undercoatings to wear and tear, washing, etc., it is necessary to use a mixture which yields a film not only possessing highly resistant properties to wear, but also sufficiently elastic to resist mechanical strains that tend to crack it.

It is now a common practice to use a mixture containing thickened linseed oil, thickened wood oil and an oil-soluble synthetic resin for this coating. In cases where a final pure white film, having a smooth brilliant gloss of good resistance to wear, is needed, *e.g.* ladies' dress belts, a mixture prepared from thickened wood oil and a pale oil-soluble synthetic resin thinned with white spirit gives excellent results. Small amounts of oil-soluble metallic soaps, *i.e.* driers, are added to all oil coatings. Cobalt linoleate is invariably used in the production of the palest films and in cases where it is important that the resultant films should not become yellow in storage or in use, although the latter effect is also governed by the nature of the oils and resins used in the coating mixture.

Leather Cloths.—These are made on similar principles to those governing the manufacture of American cloth, but the cloth used in building up the final material is usually dyed, and the coatings which are applied are coloured with pigments finely ground in oil. The cloth is finished with a matt or semi-matt surface so that the use of a hard film-forming varnish of the ordinary type is precluded. In order, however, to prevent them from becoming shabby too quickly by the use of cleaning soaps, a final coating made from thickened wood oil and a hard synthetic resin, with or without the addition of thickened linseed oil, together with the addition of a fair amount of a flattening medium, *e.g.* aluminium palmitate (a non-catalytic metallic soap), and china clay, give excellent matt or semi-matt effects.

Artificial Leather and Leather Substitutes.—Various commercial products are distinguished, for example—(1) *Artificial leather made by applying coats of cellulose nitrate lacquers to dyed cotton cloth and subsequently embossing the surfaces with designs to imitate natural leather.* Ester gum, *i.e.* the glycerol ester of rosin, is usually incorporated in the lacquer to increase its adhesive properties as well as for economical reasons. Where a high-gloss finish is needed, *e.g.* spare motor-car tyre-covers, an additional finishing coat of clear lacquer containing a suitable weather-resistant synthetic resin is applied. (2) *Artificial leather cloth built up on a rubber-coated cloth.* The finishing coats for this material need to adhere well to the rubber film and to be highly elastic; they may be coloured with pigments and, if desired, may contain flatting agents. (3) *Artificial leather cloth made from waste fibres, paper, waste leather, etc.* An elastic and tenacious binder is required for the materials, including fillers, used in making a cloth of this kind, and polymerised vegetable oils, with or without the addition of synthetic or natural resins, are universally employed. The final finished effect is produced in an analogous manner to that indicated under (2).

Oilskins, "Oiled Silk," Waterproof Gauze, etc.—The cloth for these materials is thoroughly sealed, preferably with highly polymerised types of linseed oil containing synthetic or natural resins.

Sailcloths, Fire-Hose, etc.—The essential requirements of finished hemp and cotton cloths used for making sails, fire-hose, etc., are highly efficient waterproofing, with high elasticity and freedom from tackiness. Several coatings of so-called long-oil varnishes containing synthetic resins are applied to the cloth, sufficient time being allowed between each coating to enable good penetration and drying to occur.

Heavy Waterproof Fabrics, e.g. *Tarpaulins, Canvas Roofing, Cargo and Boat Covers, etc.*—These need to possess good resistance to wear and tear, variable weather conditions and attack by mildew. They are usually finished in brown, tan, green, or dull olive shades. Heavy cloths, *e.g.* ducks, are impregnated with hot mixtures of solutions of waxes, pitches, petroleum oils, etc., in petroleum naphtha, to which pigments, *e.g.* yellow and red ochres, etc., and extenders, *e.g.* lithopone, asbestine, etc., are added as required. The heavier the cloth to be finished the lower is the amount of the finishing mixture, *i.e.* weighting, contained in the dried finished material, but in any case it rarely falls below 30%. A few special types of waterproof coverings characterised by the absence of a tacky and greasy handle, but possessing flexibility even at low temperatures, and resistance to softening on warming, are weighted only to about 20%. In such cases, mixtures of hard waxes and petrolatum, together with a little aluminium stearate as toughening medium, are often used; the ratio of the weight of the above mixture to the weight of the solvent used is calculated, after practical trials, to give the requisite degree of weighting to the finished goods.

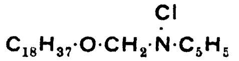
Waxes are dissolved in a petroleum fraction having a distilling range of about 265–340°F., and a flash point of 86–90°F. The impregnating solution or mixture is contained in a small steam-jacketed box, provided with three guide rollers which depress the cloth into, and guide it through, the mixture which is kept at a temperature of about 120°F. In one method, excess mixture is removed from the surfaces of the cloth by the pressure on them of blunt blades or doctors, and the cloth then passes round a few steam-heated cylinders where the solvent is removed and the liquid waxes, etc., thus penetrate deeply into the fibres and, on subsequent gradual cooling, partly fill up the interstices between warp and weft threads. The effectiveness of the latter condition is largely dependent upon the concentration of the waxes, etc., in the impregnating mixture. This method gives good penetration, but complete closure of the spaces between the warp and weft is seldom achieved. A better method is first to dry the cloth over a series of steam-heated cylinders from which it is drawn directly into the impregnating bath. On leaving the latter, it is subjected to flexing and friction by drawing it over a series of six staggered steel rollers, and the cooling effect caused by the travel of the cloth, effects an increase in the viscosity of the waterproofing medium which, in conjunction with the action of the steel rollers, yields a more fully closed waterproof effect than the method described previously. Many other variations of the methods are in use, *e.g.* the padding method, in which the cloth is squeezed as soon as it emerges from the impregnating bath. The rollers of machines of this type are often made now of synthetic rubber which is only slightly affected by the solvent in the impregnating mixture. In certain other methods, a pasty wax-impregnating mixture is applied to one or both surfaces of the cloth; the cloth is then passed over cooling rollers and dried in a hot flue.

The real effectiveness of all waterproofing methods is dependent largely on the concentration and efficiency of the water-repellant agents used, and the penetrating power of the carrying medium, *i.e.* the solvent or other dispersing agent, on the nature of the cloth to be treated, *i.e.* whether close or open mesh, and whether made from tightly or loosely spun yarns, on its weight per unit area, and the particular method of, and the type of machine used, in applying the dispersion of waterproofing materials. In general, the best methods are obtained when heavy cloths are completely impregnated with hot moderately concentrated solutions; if the concentration of the waterproofing agents is reduced below a minimum point, the effects obtained are of the porous showerproof or water-repellant type. When the waterproofing medium is applied to one or both sides of the cloth, *i.e.* the so-called coating process, the resultant continuous waterproof homogeneous films often show poor resistance to wear and tear, especially in the case of wax coatings; if the film breaks, the material soon ceases to exhibit water-repellancy. Coating methods in which solutions of wax, etc., are used, find considerable application, however, in the finishing of low-weight cloths of fairly open textures. An example of a method of waterproofing (and weighting) heavy canvas cloth for use as an out-of-doors protective covering material is as follows: 23 lb. petrolatum, m.p. 135°F., and 20 lb. paraffin wax, m.p. 124°F., are melted in an electrically heated pan; 30 lb. petroleum bitumen are added and the whole stirred until the latter has dissolved. Finally, the mixture is poured through a sieve and allowed to cool. When required for use, definite weights of the product are heated gently and thinned with varying amounts of a suitable petroleum oil fraction according to the kind of finish required, the type of canvas, etc., to be impregnated, and whether or not the material passes between squeezing rollers after leaving the impregnating box. An average concentration is about 50%. This mixture yields a brownish coloured finish which may be toned, if desired, by adding a portion of a well-ground paste of iron oxide to the hot wax-bitumen preparation. Also, extenders, *e.g.* asbestine, may be added for cheaper goods. Impregnation of the canvas is achieved by drawing it, at a speed of about 40 yards per minute, through the mixture at 116–120°F. After leaving the impregnating box, the cloth travels a short distance horizontally to the first of a series of smooth steel flexing rollers, excess mixture being removed while it is travelling horizontally by means of two doctor blades which are placed a short distance apart and caused to press upon the two sides of the cloth immediately above the impregnating box, so that excess mixture falls back into it. After passing round the steel rollers, the canvas is looped on rods and is then conveyed by chain mechanism into an enclosed drying chamber in which the temperature is maintained at 112°F.

Showerproof or Water-Repellant Effects.—Closely woven or dense fabrics invariably give better results than those of a more open structure on treatment with water-repellant substances. The oldest process, which is still used to a considerable extent, is carried out by precipitating on the fibres aluminium salts of fatty acids of high molecular weight. Thus, cotton fabric is impregnated with (*a*) a solution of good quality soap containing about 1½–2 oz. per gallon and then, after squeezing out excess liquor, with (*b*) a suitable aluminium salt, *e.g.* the acetate or formate. Operations (*a*) and (*b*) may be carried out in the reverse order. In the case of woollen and worsted cloths, which frequently contain traces of residual soap, good water-repellant effects can often be obtained merely by agitating them for some time in a scouring machine or dolly in presence of an aluminium salt, *e.g.* 8–10°Tw. aluminium acetate; if a better effect is required, the cloth is impregnated subsequently with dilute soap solution. Finally, it is squeezed and dried at an elevated temperature to induce the deposition of a basic aluminium salt and/or aluminium oleate, etc., on the fibres. Another method consists in depositing a thin coating of wax on one or both sides of the fabric by bringing them into contact with a solution of paraffin wax in petrol followed by a drying operation and recovery of the solvent. In this method, the choice of wax or wax mixture is very important in order to enable the treated material to retain its flexibility. Excellent results, however, have been obtained by this method for over 30 years, whereas the use of ordinary aqueous dispersions of wax made by crude methods of emulsification have seldom given satisfactory results. Considerable attention, however, has been paid by the large dye and other chemical manufacturers during the last decade to the principles of emulsification, and a great deal of research work has been directed to the production of stable emulsions of paraffin wax. As a result of this work, a series of proprietary water-repellant agents is available now in commerce. Several types of these products can be distinguished. One type consists of emulsions of mixtures of paraffin wax, fatty acids, etc., to which a portion of aluminium acetate or formate is added before use and the diluted aqueous mixture used in one bath, or the diluted wax emulsion may be applied to the cloth first and then, after squeezing, the aluminium salt solution; in another type, the wax emulsion already contains the requisite agent required for the proper fixation of the ingredients, and, consequently, they are suitable for use as one-bath impregnating agents. The preparation of members of both classes is dependent for its success largely on the careful control of p_H, and the use of efficient emulsifying compounds. (*v.* Emulsions, Vol. IV, p. 302*c.*)

The single-bath type of showerproofing agent appears to be gaining in popularity in actual practice, as it is more stable than the two-bath type and imparts a firmer handle to the cloth on which it is used. A treatment bath containing either type is rendered unstable in presence of certain electrolytes, especially those containing SO''_4 ions. Filling and finishing materials, *e.g.* dextrin and starch pastes, etc., may be added to the showerproofing liquor. The material to be showerproofed with these products is simply impregnated by working it in the diluted emulsion, *e.g.* about 5% on the weight of the material, for some time, followed by hydro-extracting and drying; piece goods may be impregnated by padding, *i.e.* passing them in continuous lengths through a small box containing a dispersion of the agent in the proportion of about 1:16 of water; the pieces are squeezed immediately as they are drawn between two rollers placed vertically above the liquor box, and dried by hot air.

"*Permanent*" *Water-repellant Effects exhibiting a Soft Handle.*—One of the latest developments in the search for new water-repellant substances is the discovery (*cf.* B.P. 466817, 469476 and 477991) that quaternary ammonium salts obtained from halogenomethyl ethers of long-chain higher fatty alcohols or amides and pyridine, *e.g.*



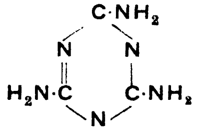
$$C_{18}H_{37}\cdot O\cdot CH_2\cdot \overset{Cl}{N}\cdot C_5H_5$$

and

$$C_{17}H_{35}\cdot CO\cdot NH\cdot CH_2\cdot \overset{Cl}{N}\cdot C_5H_5,$$

yield, when applied to fibres and then heat-treated, valuable water-repellant soft finished effects which are stable to washing and dry cleaning. These new products, upon which the commercial substances known as "*Velan PF*" and "*Zelan A*" appear to be based, decompose, on heating strongly, with liberation of pyridine; if decomposition takes place, for example, in presence of cotton, an insoluble hydrophobic long-chain fatty residue intimately associated with cellulose is obtained. Some chemists consider that chemical interaction between the hydroxyl groups of cellulose and the long-chain fatty residue occurs, but there is no real evidence that such a complex is formed. The clean material, *e.g.* cotton free from sizing, filling, etc., to be showerproofed, is impregnated in a manner best suited to its physical state, with an aqueous solution of Velan PF at 40°C. It is then squeezed, dried quickly in a rapid current of hot air to prevent premature decomposition of the compound, followed by heating (baking) for a few minutes at about 140°C. Finally, the cloth is washed in a solution of a mild alkali (soaped), rinsed, dried, and finished as required. Other fibres, including wool and silk, yield similar effects, but the temperature and time of the baking process need to be modified according to the degree of susceptibility of the particular fibres to heat-tendering and/or discoloration. Many other patents for the use of complex water-repellant compounds, *e.g.* highly reactive *iso*cyanic, *iso*thiocyanic and carbonic esters of high molecular aliphatic alcohols (*i.a.* B.P. 130277, 461179), have been granted in recent years, but, as most of these compounds appear to give the best results when applied as solutions in organic solvents, their utility is somewhat limited in textile processing, although aqueous dispersions may be used in the impregnating operation. It has been suggested that *iso*cyanates of general formula $R\cdot N\cdot CO$, in which R=a long chain aliphatic group, *e.g.* stearyl*iso*cyanate combine with cellulose chemically but, in these cases, also, the evidence available is not sufficiently definite to warrant this assumption. Water-repellant effects on most cellulosic fibres are obtained with the new compounds by the normal procedure, viz., impregnating, squeezing, and drying at elevated temperature until the reaction is complete.

Another type of modern water-repellant agent is produced by impregnating textile fibres with a mixture which, on subsequent heating, undergoes polymerisation *in situ* to a water-insoluble compound. Amongst these compounds are mixtures of long chain aliphatic derivatives of urea, *e.g.* octadecylurea, with formaldehyde, which first form methylol condensates, *e.g.* $C_{18}H_{37}\cdot NH\cdot CO\cdot NH\cdot CH_2\cdot OH$, and then, on subsequent heating, polymerise to yield complex insoluble compounds. Mixtures of melamine,



and formaldehyde also yield finished effects fast-to-washing after heat-hardening (*cf.* B.P. 466015). Many other mixtures, which behave in a somewhat analogous manner, have been patented, but their uses in finishing textile fabrics are in the early stages of exploitation.

Flameproofing Cotton and Rayon Fabrics.—It is well known that most textile fabrics are liable to burn more or less quickly in air on application of heat, whereby the temperature rises to a point termed the ignition point. Sometimes spontaneous ignition occurs owing to the presence on the fibres of thin films of semi-drying vegetable oil; this phenomenon is due to auto-oxidation induced by the presence of unsaturated carbon bonds in the oil molecules. In general, those fibres which are free from natural impurities are more inflammable than raw fibres, whilst the physical form of the material is a determining factor in assessing the degree of inflammability. Thus, cotton flannelette, *i.e.* cotton cloth with a raised fluffy surface, is much more liable to take fire in presence of a flame than is a piece of ordinary cotton cloth. Also, cellulose fibres take fire more readily and burn more rapidly than do protein fibres. Methods of reducing this dangerous attribute of fibres have been in use for generations. The oldest method is to incorporate suitable inorganic salts with the finishing paste or mixture applied to cloths before the dry finishing operations, or in cases of structures which need to remain soft and supple, *e.g.* fine cotton fabrics, rayon fabrics, etc., with solutions of inorganic salts alone. Ordinary ammonium salts, *e.g.* ammonium chloride, phosphate and sulphate, have been in use as flameproofing agents for many decades, as also have borax, boric acid, disodium hydrogen phosphate. Simple impregnation of fibres with water-soluble salts of the kind mentioned, followed by drying to remove excess water, yields a flameproof effect which, of course, is not permanent, *i.e.* it is not fast-to-washing, so that when fast-to-washing flameproof effects are required, it is customary to modify the process in order to bring about the precipitation in the fibre of insoluble metallic salts or oxides, *e.g.* aluminium phosphate or silicate, stannous tungstate (from sodium tungstate and stannous chloride), zinc compounds, etc. Whichever method is adopted, the same initial procedure is adopted; the cloth is impregnated on a padding machine with a solution of the substance or substances chosen, followed by drying. If the deposition of an insoluble salt is required, the treated cloth is next impregnated with a water-soluble salt containing a positive ion which is capable of interacting with the negative ion of the salt already present on the cloth, to produce the required product. Thus, if the first salt is disodium hydrogen phosphate, the second may be aluminium acetate. Cloth which has been treated with these salts is allowed to lie for some time and then dried on steam-heated drums. If excess aluminium acetate is used, a final soaping of the cloth yields aluminium soap which helps to preserve the flameproof effect against repeated washing. Mixtures of borax and boric acid give excellent results, but, in cases of dyed goods, it is necessary to use products that do not alter the shades. Recently a very simple treatment, consisting in the use of solutions of ammonium sulphamate, has been introduced. Over 100,000 yards of fabric employed at the New York Fair, 1940, were flameproofed with this compound.

The substances enumerated are also suitable for flameproofing rayon fabrics. An interesting development is the addition of flameproofing agents to the solutions used in " spinning " artificial fibres. Several recent patent specifications dealing with the formation, *in situ*, of complex organic or semi-organic condensates, appear to indicate the trend of much work being carried on in the search for a satisfactory flameproof finish for cellulosic materials.

Crease-Resisting Finished Effects.—It is a matter of common observation that cellulosic fabrics tend to crease readily when non-uniform layers of material are subjected to strain; moreover, the creases are not easily removed in contrast with analogous effects on wool and silk fabrics. The latter, therefore, are said to possess the property of recovering more or less quickly from physical deformation, *i.e.* in comparison with cellulosic fabrics, silk and wool structures exhibit the phenomon of elastic hysteresis only to a small extent. The scientific explanation of this difference is intimately connected with differences in molecular structures which, in the case of cellulosic materials, leads to a dissipation of some of the energy of deformation. (This aspect of the subject is best considered in connection with a study of modern views on the molecular structures of fibres as deduced by specialist workers in organic chemistry and in X-ray diffraction analyses). Practical methods of rendering cellulosic fabrics crease-resistant in an economical manner began to attract the attention of textile chemists in 1928 (*cf. also* p. 191*d*), when certain patent specifications commonly known as the Tootal patents (*cf.* B.P. 291473, 291474, 304900, etc.) were published. These refer to the use of resinous urea- and phenol-formaldehyde partial condensates produced *in situ* on the cloth to be rendered crease-resistant. A large number of other substances and methods, designed to produce these effects as well as combined crease-resistant and water-repellant, etc., effects, have been patented during recent years, but the original process still appears to be the most widely used. Since phenolic condensates tend to give yellowish semi-brittle effects, it is the invariable practice now to use the urea-formaldehyde process, which is carried out by impregnating cellulosic fabrics, preferably in a swollen or semi-swollen state with a solution containing urea and formaldehyde in presence of an acid catalyst followed by drying, cooling and finally baking (condensation) at about 150°C. Boric, tartaric, etc., acids may be used as catalysts. Thus, cotton cloth, which has been scoured with soda ash and soap, bleached with calcium hypochlorite solution, rinsed until free from residual chemicals and dried well, is impregnated on a padding machine with a solution containing 20–30% of 40% formaldehyde, 10% of urea and 0·75% of tartaric acid, and excess liquor removed either by means of two small-diameter squeezing rollers or a suction hydro-extractor, dried as rapidly as possible, cooled, subjected to a heat treatment at 150–160°C. for a short time, washed in hot soap liquor, rinsed well and dried. Combined crease-resistant and waterproof effects (*cf.* B.P. 413328) are obtained by first impregnating cloth with aluminium acetate solution, squeezing and heating; the cloth, which now contains aluminium hydroxide, is then treated, as already outlined above, with an initial condensate of resin components, soured, rinsed, dried, heated at 170°C. for two minutes, soaped, rinsed and dried. Viscose rayon which has been treated in this way does not leave weals or edges if spotted with water, whereas ordinary viscose rayon leaves objectionable marks. Condensates of stearamide and formaldehyde and certain complex quaternary ammonium salts, etc., have also been suggested for the production of crease-resistant, spot-proof finished effects.

MULTIPLY FABRICS.—A few years ago a method of producing multiply fabrics by utilising cellulose acetate fibres as bonding agent was introduced. Shortly afterwards so-called "*Trubenised*" collars, cuffs, etc., appeared in commerce. In the original manufacture of multiply fabrics of this type, two layers of cotton cloth containing cellulose acetate rayon threads were placed one on top of the other and then ironed or calendered at about 200°C.; at this temperature the cellulose acetate threads become sticky or resinous (owing to their thermoplastic property) and adhere tenaciously to the interior and adjacent threads of the superimposed fabrics so that a permanently bonded fabric is obtained. At a later period it was found that bonding could be achieved more efficiently by carrying it out in presence of liquid swelling agents for the cellulose ester; in another modification, a thin film of cellulose acetate is interposed between two layers of cotton and bonding effected as described. Many other patent specifications relating to the production of multiply fabrics have been granted; as a rule they refer to the uses of different thermoplastic compounds as bonding agents. One of the most promising methods is carried out by coating a fabric on one side with a solution of a synthetic resin, *e.g.* a solution of a polymer of methyl methacrylate in toluene. After drying to remove toluene, the coated fabric may be stored until required. In actual manufacture of multiply fabrics from this material, layers of ordinary fabric are superimposed on one another with layers of the coated fabric between them and the whole hot-calendered to bind all the layers into one compact assembly.

Aqueous emulsions of special synthetic resin polymers are also available now for use in the manufacture of multiply fabrics.

Finishing Rayon Cloths.

In considering the practice of finishing rayon cloths it is important first to note that the progress made in their construction during the last decade has resulted in the introduction of scores of differing fabric types as regular articles of commerce. For example, in addition to constructions consisting of 100% viscose rayon, 100% cellulose acetate and 100% cuprammonium rayon respectively, a large number of cloths containing (*a*) two kinds of rayon, (*b*) rayon and cotton, (*c*) rayon and silk, etc., are of great importance, as also are rayon fabrics woven partly, or entirely, from spun rayon, *i.e.* fine raw filament rayon which, after having been cut into short lengths and purified, etc., has been spun into yarn in an analogous manner to that used for spinning raw cotton. Apart from the nature of the fibres present in warp and weft yarns used in weaving the various fabrics, the physical forms of the yarns and the constructions or weaves employed mainly determine the trade names given to the commercial types of fabric manufactured. Most rayon or mixed rayon fabrics are of the plain weave type, the best known being termed twills, satins, chiffons, voiles, crêpes, etc. Amongst the most important of these, at present, are the various kinds of crêpe fabric, rayon-cotton linings, twills, etc.

It is probably true to say that no type of fabric made from natural fibres demands the exercise of so much care in wet processing operations, as well as in the final finishing operations, as do rayon goods. Even if the fact that modern rayon fabrics are of widely different constructions is ruled out, it has always to be borne in mind that ordinary wet rayon is about 50% lower in strength than the dry fibre, whilst even a higher diminution in strength is shown by spun rayon when wet. All types of rayon fabrics, therefore, are very susceptible to deformation if subjected, while wet, to high strains and stresses, with the inevitable development of faults of a specific kind. Consequently, it is the general practice to use wet-processing machinery specially designed to impose as little strain as possible on the fabrics during treatment. The main work of the rayon finisher is usually directed towards the production of fabrics possessing softness and good draping properties, although stiffness can be easily imparted whenever required.

100% *Viscose Rayon Fabrics.*—Fabrics of open construction and those made from loosely spun yarns are usually processed on jigs or padding machines. The pieces of cloth, after having been marked at each end for identification purposes, are wound on to shells or beams, care being taken that no creases are introduced; each beam may contain several hundred yards of cloth. If the warp threads contain starch (used in sizing them before weaving), the cloth is passed first through a weak solution of malt extract or other desizing agent at about 140°F. and, if considered advisable, the cloth is allowed to stand for a short time so as to ensure conversion of the starch into water-soluble products. The cloth is next washed in water and scoured in a boiling solution of soda ash and soap, washed again, dyed, rinsed, treated with a weak solution of a softening agent, hydro-extracted in open width and dried; it is then dampened with steam, dried on a stentering machine, passed through a Palmer machine (*see* p. 201*c*) and finally calendered on a light 3-bowl machine. In the modern manufacture of 100% rayon fabrics, it is customary now to use gelatin instead of starch in sizing the warp threads; this type of size is readily removed in the scouring operation, or a preliminary treatment with a hot solution of a proteolytic enzymatic preparation may be carried out.

Other 100% viscose rayon flat goods, *e.g.* twills, taffetas, sateens, etc., are prepared, dyed and finished in an analogous manner. Fabrics of spun viscose rayon (staple fibre) are usually treated in rope form during scouring and dyeing, and, as starch is generally present on the warp threads, a careful desizing treatment is essential. As already mentioned, the pronounced weakness of wet goods containing viscose staple fibre demands that they should receive the minimum amount of handling. Slow drying and not too much tension during stentering of the hydro-extracted cloth result in the development of excellent finished effects.

Viscose Rayon–Cotton Fabrics.—Many fabrics of this type, *e.g.* so-called "alpacas," warp-striped (rayon) poplins, warp- and weft-striped (rayon) shirtings, etc., were formerly scoured, etc., in rope form with 3°Tw. soda ash solution and 2% soap in kiers at 180–200°F. for 5–6 hours. In modern scouring practice, however, it is customary to carry out the process continuously in batteries of machines designed to draw the cloth in slack form through the scouring liquor contained in boxes, above which are oval-shaped reels, and to subject it to intermittent squeezing between rubber-covered rollers. The cloth is singed first, then desized and passed through hot water contained in the first box of the machine; it is next drawn over a reel, squeezed between rollers and entered into scouring liquor (second box) consisting of about 1·5% soda ash and 2% soap (on the weight of the cloth), together with a small amount of an emulsified solvent. Fresh scouring liquor is added regularly from a stock supply tank; after passing over the second reel, the cloth is squeezed again and drawn forward through another scouring liquor contained in the third box, squeezed and so on; the third and fourth boxes contain hot and cold water, respectively. Finally, the cloth is scutched (opened out), mangled (squeezed between a pair of rollers, one of which is brass and the other covered with rubber), and dried on steam-heated cylinders. If desired, the cloth is then impregnated with a weak solution of a softening agent, squeezed well, dried and stretched on a stenter, passed through a Palmer finishing machine (*see* p. 201*c*) and lightly calendered. Many variations of this procedure are used to suit the different types of fabrics or to utilise existing plant installed in the works.

Union Linings containing Rayon.—These are usually woven with a viscose rayon warp and a cotton weft; or they may be made of 100% cellulose acetate rayon. Linings are commonly wet-processed in open width; those consisting of viscose rayon and cotton undergo treatment similar to that described in the preceding paragraphs.

100% *Cellulose Acetate Rayon Cloths.*—Flat cloths, *e.g.* satins, taffetas, linings, etc., are often processed as follows:

INSPECTION, SEWING AND BEAMING.—The cloth is first examined for obvious defects, *e.g.* tears, stains, etc.; an end-cloth, a few yards long, is then sewn to one end of the first piece of cloth; the end of the latter is next sewn to the upper end of the second piece, and so on, until the requisite number of pieces for collective treatment have been assembled; finally, an end-cloth is sewn on to the end of the last piece of cloth in the assembly. The first end-cloth is then wrapped round the wooden shell of a beaming machine and the machine set in motion. As the cloth is slowly and very carefully wound on to the shell it is examined for defects which are noted carefully for future reference. The batched, rolled or beamed cloth must be free from creases; in some cases it is best to re-wind the cloth on to a second shell or beam so as to ensure freedom from creases and to make the selvedges at the sides of the beam perfectly even.

SCOURING OR BOILING-OFF.—The beam is placed on a jig and the cloth on it drawn through cold water contained in the trough of the jig and beamed on another shell on the opposite side of the jig; in this operation, particular care is exercised in the judicious use of expander bars in order to make sure that all creases are eliminated. Light-weight cloth is then drawn through a solution (about ⅛% concentration) of a suitable commercial enzyme preparation at 140°F., and wound on to the jig roller, the operation being repeated about four times; one passage through the liquor of the whole of the cloth is termed an "end." A solution of good quality soap, usually with addition of a higher fatty-alcohol sulphate, so as to give a soap concentration of about 1% and ⅛% fatty alcohol sulphate, respectively, is then added to the bath. The cloth is passed through the liquor at about 120–140°F. for 4–6 ends, the liquor discharged and the cloth rinsed in warm water, when it is ready for dyeing. The scouring liquor ingredients are varied from time to time according to the nature of the cloth to be processed. Thus, an emulsion of xylene with Turkey red oil and soap is often used for light goods, especially when they have to be bleached; the treatment in such cases may begin at a low temperature (the desizing liquor having been discharged) and gradually increased to not higher than 180°F. for bright finished, and 200°F. for dull lustre, goods. Bleaching, if needed, is carried out by passing the cloth for 6 ends at ordinary temperature through a very weak solution of acidified sodium hypochlorite at p_H 5·5, approx. [about 3 pints sodium hypochlorite solution (20% available chlorine) and 4 pints 40% acetic acid per 90 gallons water]. The cloth is then rinsed in cold running water, passed through weak sodium sulphite solution to remove traces of chlorine, rinsed in warm water, and tinted (4–6 ends) at 160°F., in a 0·1% solution of a suitable bluish-violet cellulose acetate rayon dye containing a little sulphated fatty alcohol and made slightly alkaline with borax. If bleaching with hydrogen peroxide is preferred, satisfactory results are obtained by passing the cloth (4–8 ends) through a 0·0025% hydrogen peroxide solution, at 180°F., rendered slightly alkaline with sodium silicate, followed by rinsing in hot water; tinting may be carried out as described above. Finally, the cloth is passed through very weak acetic or formic acid and is then ready for dyeing and/or finishing.

If it is desirable to impregnate the cloth with a special finishing compound, *e.g.* a softening agent, this operation is sometimes carried out by passing the cloth (a few ends) through a warm solution of the selected compound. At this stage, the cloth, whether dyed or not, is vacuum extracted on a machine provided with fine slotted suction pipes usually arranged in staggered, serried lines against which the cloth passes when drawn at width through the machine from one beam to another. This method of removing excess water is finding increased favour and some modern jigs are equipped with an apparatus of this kind, since its use at various stages in wet-processing operations tends to reduce the number of ends normally required when using ordinary jigs. As previously mentioned, if it is necessary to apply a finishing agent to the cloth in order to obtain finished effects characterised by special softness, draping properties, etc., the application may be done in the jig immediately after the vacuum extraction (*see above*); or a padding machine provided with two or three squeezing rollers according to the pressure required may be used. The softening agents in general use are weak solutions of sulphonated fatty oils, sulphated higher aliphatic alcohols, certain types of condensation products containing long chain aliphatic radicals, emulsified fatty oils, etc. Also, it is often advisable to add small amounts of hygroscopic substances, *e.g.* ethylene glycol or mixtures of this substance and glycerol to the liquid, the p_H of which is controlled so that it only varies between narrow limits, *e.g.* 5·0–7·5. Impregnation of heavy cloth is carried out on the padding machine, and small quantities of stiffening substances, *e.g.* gum Tragasol, may be added to the softening mixture.

Modern Rayon Finishing Equipment.—The finishing equipment used in the final processing of rayon and rayon-containing fabrics often consists of (*a*) an impregnating or padding machine for applying finishing compounds, *e.g.* softening agents, etc., as previously explained; (*b*) apparatus for removing excess water, *e.g.* a series of steam-heated drying cans or drums, or vacuum hydro-extractors; (*c*) stentering or tentering frame; and (*d*) a Palmer finishing machine.

Stentering frames are used to ensure that the weft threads are arranged at right angles to the warp threads in the finished fabric and also to fix the width of the fabric as required. A modern high-speed stenter may be 40 ft. long; it is provided with large enclosed steam coils for partly drying the cloth as it passes along the machine; at the outlet end, the cloth is released automatically from the endless chains of clips of the machine and passed directly to a Palmer finishing machine.

A range of the type indicated, *i.e.* (*a*), (*b*), (*c*) and (*d*), is usually operated as one unit by means of a variable speed drive and compensating mechanism to prevent excessive pull on the cloth while it is passing from one unit of the range to another unit. The Palmer finishing machine consists of (i) one large and one small steam-heated drum, and (ii) a beaming arrangement for winding the dry finished cloth on to a shell. The periphery of the large drum is covered with an endless woollen blanket or apron; this apron is, itself, covered to about 75% of its contact with the drum, with an outer endless blanket, which, when the machine is in use, travels also round the small heated drum in order to remove the moisture absorbed by the felt from the damp cloth undergoing treatment. Cloth which is to be finished on the Palmer machine is drawn forward by the large revolving drum and passes round it while held firmly between the two blankets; and, at the exit, the cloth is wound on to a shell. The temperature of the large drum is usually kept at about 220°F., and its speed which, of course, will be the same, approx., as that of the whole range, may be varied from 30–60 yards per minute.

CALENDERING.—A standard rayon calender consists of three bowls or rolls supported vertically and held in a steel frame. The top and bottom bowls are covered with wool-felt paper and the middle bowl, which can be heated internally, is of steel or chilled iron. Means are provided for varying the pressure at the points where the top and bottom bowls are in contact with the middle bowl. Most rayon fabrics are calendered cold under light tension and pressure; the average speed of the cloth when passing through the calender is about 50 yards per minute. When a lustrous finished effect is required, the middle bowl is heated and the pressure on the travelling cloth increased. Ordinary light calendering helps to improve the draping properties and handle of the cloth; it also tends to " break up " the surface, thereby inducing a dull finished effect.

NON-SLIP (RESIN-) FINISHED EFFECTS.—Rayon fabrics easily fray and slip when subjected to strain either warp or weft way; many types of twills, taffetas, satins, etc., are particularly susceptible to the development of these defects and, consequently, they have poor wearing properties. It has been discovered in recent years, however, that such defects can be prevented by the application of a suitable synthetic resin finish to the cloth. This technique recalls that used for producing anti-crease fabrics (*see* p. 198*d*), but in the latter case, about 10% resin on the weight of the cloth is required and it needs to be deposited within the fibres, whereas in the production of a non-slip resin-finish, about ¼–1% resin gives satisfactory results, since its purpose is merely to act as a bonding material for the warp and weft threads at their surfaces only. The most suitable resin to use appears to be a urea-formaldehyde condensate, but other substances capable of bonding the fibre surfaces can be used. The dry cloth (scoured, bleached and/or dyed) is impregnated with the " resin " solution, squeezed, stretched and dried on a stenter at the required width and finally heated at a high temperature. The finished effect should prevent the fibres from fraying and should be fast to repeated washing, dry cleaning and hot pressing. The resin treatment may be extended, in certain cases, to set or stabilise the fibres in fabrics. Thus, fabrics made from staple fibre tend easily to stretch, sag and shrink in use, but if they are treated with a resin solution (equivalent to 1½–2% resin on the weight of the cloth) and the resin " cured " as outlined above, they become not only resistant to abrasion, but are stabilised against the defects enumerated above.

When the resin has been " cured," the fabrics may be subjected to other finishing operations in order to subdue the slightly harsh " handle " that may be caused by its presence. Resin-finished effects may also be produced on other kinds of fabrics.

DELUSTRING OR MATTING PROCESSES.—In the early days of the rayon industry, the usual finished effect on rayon fabrics was of a lustrous type. In some cases, *e.g.* viscose-rayon fabrics, the finished effect was often described as having a metallic lustre which, in addition to the fact that such an appearance envisaged the lack of warmth, inevitably led to the view that it did not accord with æsthetic principles as applied to articles of dress.

Hence, after the early period of development in the rayon industry, there arose an insistent demand for fabrics exhibiting subdued lustre, *i.e.* a lustre more approaching that of, or even considerably less than that commonly exhibited by silk goods. At first it was customary, as is often the case now, to matt or delustre rayon fabrics during the finishing process, but rayon manufacturers also gradually modified their " spinning " technique so that, to-day, yarns of widely differing degrees of lustre can be purchased for weaving or knitting purposes (*see* FIBRES ARTIFICIAL, this Vol., p. 128*b*).

Delustring or matting lustrous fabrics may be accomplished in various ways. Thus, the lustre of ordinary cellulose acetate-rayon fabrics is considerably reduced if the fabrics are treated, without tension, with boiling soap solution for some time. The dulling effect, in this case, is accelerated by the presence of a little phenol, but it is essential to maintain the p_H of the bath within narrow limits; dulling is inhibited if the material is treated while in a stretched condition. Conversely, the dull effect, obtained as indicated, reverts to the lustrous type if the fabric is dry-steamed or heated under pressure in presence of a swelling agent.

The readiness with which cellulose acetate-rayon fabrics are delustred depends to a considerable extent on the actual manufacturing process used in making the yarns. Thus, if certain substances, *e.g.* alkyl esters of higher fatty acids, are present in the spinning dope, the resultant dry-spun threads quickly acquire a uniform delustred appearance when treated in hot soap solution; a similar, but more pronounced, effect occurs if titanium oxide is dispersed in the spinning dope. Many other substances have been advocated for addition to the dope so as to obtain delustred filaments directly on " spinning." When cellulose acetate yarns having different physical properties are present in a fabric, it is possible to obtain uniform dull finished effects by subjecting the fabric to a preliminary oxidising action with dilute hydrogen peroxide followed by the usual hot soap treatment.

Lustrous viscose-rayon fabrics are often matted during the finishing process by impregnating them with an aqueous dispersion of china clay, zinc oxide, titanium oxide, etc., previously emulsified with soap, glue, etc. Permanently dull effects are obtained on both viscose and cellulose-acetate rayon fabrics by treatment with a solution of a suitable silicofluoride in such a way as to induce the deposition, by hydrolysis, of silicic acid, which is partly dehydrated on drying.

One of the most interesting problems concerned with delustring methods applicable to cellulose acetate-rayon goods is due to the difficulty of obtaining satisfactory results on fabrics dyed in dark shades, especially blacks and dark blues. If, for example, an ordinary fabric which has been matted with hot soap solution is dyed a deep black, a large number of dye particles are deposited on the surfaces of the fibres and it is possible that the porous structure apparently developed by the delustring operation is thereby " filled up," thus restoring the lustre.

FINISHING CRÊPE FABRICS.—Fabrics showing crêpe or raised pebble effects and made from natural fibres, especially silk, have been known for several decades, but it is only within the last 10–12 years that rayon crêpe fabrics have been developed to such an extent that they rank now as highly popular fabrics for the dress-goods trade, whilst they are finding increased use as furnishing fabrics.

In order to understand the principles involved in finishing crêpe fabrics, it is necessary first to consider certain points relating to their manufacture. It is a matter of common observation that if a dry string or a series of parallel strings is twisted about its longitudinal axis, it tends to untwist as soon as the twisting force is removed; if it is wetted out thoroughly, while held in the twisted state, however, the individual filaments swell and, on removing tension, untwisting begins and proceeds to a greater extent than in the case of twisted dry fibres.

In the manufacture of crêpe fabrics, highly twisted yarn is generally used for the weft and a low twist yarn for the warp. The torsional energy introduced into the weft, or crêpe yarn, during throwing (twisting) remains quiescent as long as the fabric is kept in the dry state; if it is wetted, however, as in the initial finishing operation, the torsional energy of the crêpe yarns is partly released, whilst the fabric as a whole is able to shrink. Moreover, as the horizontal ends of the crêpe yarns are held taut at the selvedges, it follows that this release (untwisting) combined with the well-known associated phenomena, *e.g.* elasticity, creep, turgescence, etc., induce these yarns to contract and develop " snarls " or loops whereby the whole of the fabric structure is modified in such a way that it exhibits a broken irregular surface, the raised portions of which are commonly termed crêpe or pebble effects. In the modern finishing of crêpe fabrics, it is essential that these effects shall be uniform in every respect, hence exceptional care has to be exercised during the actual manufacturing operations if satisfactory results are to be obtained in the subsequent finishing process.

As previously stated, the crêpe yarns are usually weft yarns. The twist in these may be either in one direction only or, as is more usual, the weft may be built up of two threads twisted in one direction, alternating with two threads twisted in the opposite direction, *e.g.* as used in weaving canton, antique, marocain, crêpe-de-chine, etc., crêpe fabrics. Some chiffon fabrics are made entirely of crêpe yarns twisted only in one direction, whilst others, *e.g.* crêpe georgette, are made from yarns with right and reverse twist in both warp and weft.

Crêpe yarns are usually made of viscose rayon or silk (although any other fibre may be used) and the twist, *i.e.* turns per inch, varies from about 40 to 60. In order to facilitate the throwing (twisting) operation and to aid the retention by the yarns of the torsional energy introduced until the fabric, for which they are used, is ready for finishing, it is necessary first to steep the ordinary yarn in a solution containing a lubricating agent, *e.g.* an emulsifiable vegetable oil, and a substance which acts as a reinforcing and protecting agent, *e.g.* gelatin. The usual procedure in producing crêpe yarns is as follows : Skeins of ordinary yarn are soaked for a short time in a warm solution containing, for example, gelatin, dextrin and sulphonated olive oil, then hydro-extracted, opened out, dried carefully, wound on to spools, thrown, *i.e.* twisted, steamed at low-pressure for a few hours to set temporarily the twist in the yarn, conditioned for several hours and rewound on to spools. The yarn is then ready for use in weaving crêpe fabrics.

Crêpe fabrics are now made in a wide variety of types and it is not practicable to discuss here the finishing details best suited for each type. Only a general account of crêpe-fabric finishing, therefore, is given. Perhaps the most popular of all rayon crêpe-fabrics, at present, are those woven with a bright or dull cellulose acetate-rayon warp and viscose-rayon crêpe weft.

FINISHING CRÊPE FABRICS (CELLULOSE ACETATE-RAYON WARP AND VISCOSE-RAYON CRÊPE WEFT.)—The first three operations, viz. inspection, sewing and beaming are similar to those already described (*see* p. 200c) ; a flat sewn seam is essential.

EMBOSSING.—Up to a few years ago it was customary to enter rayon crêpe-fabrics directly into the " boil-off " or crêping bath according to the long-established practice of finishing silk crêpes, but in this system many defects developed, particularly uneven crêpe or pebble effects, " break " marks, etc. Uneven crêping is prevented now by first drawing the cloth continuously from a roll over a copper steaming roller and then between a pair of rollers under pressure (embossing calender) ; the top roller is made of steel with a hollow centre so that steam can be introduced to heat the roller ; its periphery is engraved either with a fine or coarse pebble design and, at the point of contact between the two rollers, the pattern on the heated roller (250–270°F.) is impressed on the cloth, thus exerting a definite control in preventing those defects caused by variation in tension set up during the manufacturing operations. Thus the desired pebble effect ultimately induced is directed along the lines of the embossed pattern. The lower pressure-roller has a steel centre upon which is built a felt-paper composition ; the two rollers are geared together so as to ensure that the impressions made by the embossed roller on the travelling cloth also fall exactly in the same places on the periphery of the bottom roller, thereby preventing overlapping of the design. Full development of the pebble or crêpe effect takes place in the next two operations known technically as " boiling-off " and scouring. The former name is derived from the " boil-off " or degumming operation practised in the silk industry, but the objects in the two cases are quite different.

The initial operation of the actual crêping process consists of the instantaneous and uniform wetting-out of the fabric ; also the size on the warp threads begins to soften and that on the crêpe yarn to dissolve. These effects allow the weft yarn to shrink as required and to move easily in contact with the lubricated warp threads, *i.e.* threads lubricated by the presence of softened size. Subsequently, the latter is removed and crêping completed in the scouring operation which immediately follows the initial wetting-out operation.

The manipulation of the fabric in crêping varies considerably according to the nature and structure of the cloth and the types of machines available. High-class fabrics are often suspended (open width) in 40 in. lengths in the crêping liquor. Suspension is achieved by means of strings sewn to the selvedges and attached to poles which rest on either side of a rectangular crêping box. This method is slow and depends for much of its success on the personal factor. The most up-to-date method is conducted on a continuous crêping-machine as follows—Fabric, in open width, is drawn, under mild tension, round and under a drum, the lower portion of which dips in the crêping liquor ; the film of liquor thus carried by the drum wets out the cloth evenly and starts the crêping action. As the fabric leaves the drum, it comes into contact with the bulk of the liquor in the tank and is caused to float through it to the delivery end of the tank or to travel through it on an open-width conveyor. The cloth is then drawn forward to the scouring machine, through which it passes in rope or semi-full-width form. This machine is often divided into series of compartments above which are placed revolving elliptical-shaped reels; each section of the machine is used for a specific purpose, *e.g.* (*a*) scouring at about 180°F., (*b*) second scouring in clean liquor at a slightly lower temperature, (*c*) rinsing in hot water, (*d*) rinsing in warm and (*e*) cold water. Usually the liquor in each section is caused to circulate in the same direction as the cloth, while the latter moves progressively from dirty towards clean scouring liquor and finally to hot and cold water. After scouring, the cloth is separated at the sewn ends and is ready for bleaching and/or dyeing and dry finishing.

A typical crêping liquor contains the following ingredients in the respective concentrations: 1% good quality oil soap, $\frac{3}{16}$–$\frac{1}{4}$% soda ash, $\frac{1}{8}$–$\frac{1}{4}$% sulphated fatty alcohol and $\frac{1}{8}$% wetting-out agent; a typical scouring liquor contains $\frac{1}{2}$% good quality soap, $\frac{1}{4}$% tribasic sodium phosphate and $\frac{1}{8}$–$\frac{1}{4}$% sulphated fatty alcohol. Sufficient amounts of these substances are added from time to time to maintain their scouring efficiency and requisite p_H, but ultimately the baths become so dirty that they have to be replaced by fresh liquors.

Bleaching and Dry Finishing.—Goods to be finished white or which have to be dyed in delicate shades, are usually bleached. Immediately after crêping, therefore, the cloth is scoured again with soap at about 180°F. for 30 minutes, rinsed well and cooled slowly. It is next bleached with sodium hypochlorite or hydrogen peroxide as described on p. 201*a* in connection with the finishing of 100% cellulose acetate rayon goods, and tinted in a fresh liquor containing a little of a mixture of a dye for cellulose-acetate rayon and Acid Violet, 4BN, for the viscose-rayon weft. The last series of operations, which is often known collectively as dry finishing, includes the following—Hydro-extracting; opening-out of the cloth to its full width and sewing the pieces together; drying on a slack or loop drying machine; first stentering or framing operation to impart initial width to the cloth (the cloth is passed over a steaming roller before it is stretched so as to simplify the operation and to remove creases); impregnating with a warm or hot solution of a sulphonated oil (or with a mixture of the latter and an emulsified synthetic resin in the case of fairly heavy crêpes which need to possess a permanent finished effect with a soft handle) on a padding mangle followed by squeezing; drying; stentering or framing to requisite finished width; calendering (this operation is usually needed for cloth which has been impregnated with a solution containing modified starch, gum, etc.). "Decatising," which is sometimes substituted for calendering, tends to eliminate many of the defects, *e.g.* too much lustre, harsh feel, non-uniform pebble effect, etc., that develop in previous operations. It is carried out as follows—About 300–500 yards of fabric are wound, in contact with a blanket interlay, on to a perforated cloth-covered drum. High-pressure steam is caused to pass *via* the drum and its perforations through the layers of material for a short time; as a result, the fibres become turgescent and, consequently, more easily mouldable, and this phenomenon combined with the pressure of the blanket interlining tends to reduce gloss and give a more uniform pebble effect. When the steam supply is shut off, a partial vacuum is formed in the drum whereby cool air is sucked through the layers of cloth and excess moisture (from condensed steam) removed, but, at the same time, sufficient moisture is left in the cloth to yield conditioned material fully equal to that which has been conditioned in air. Finally, the fabrics are inspected, measured and made up into rolls, etc., for sale.

E. C.

FINISHING OF WOOLLEN AND WORSTED FABRICS.—The term "finishing" broadly applies to processes carried out on fabrics subsequent to weaving, and terminating with complete fitness for use. Prior to the present century it was almost entirely empirical, a system of operations developed from practical arts originated by trial and error tempered by observation and experience. Only in recent years has it received theoretical attention. To some extent it is now possible to develop its methods from a basis of scientific principle and, for this purpose, account must be taken of the intrinsic properties of the raw material—wool substance and fibre—and thereafter the principles of physics, chemistry and engineering are involved.

The *wool fibre* belongs to the animal textile fibres and is unique in its totality of properties. *Keratin*, the particular sclero-protein of wool yields as the most characteristic degradation product *cystine*, distinguished by its sulphur content. The protein molecules, as investigated by X-ray analysis, are assembled into elongated micellar chains cohering laterally through their side chains, the cystine linkage being the most characteristic of these. Physically these chemical protein micelles are aggregated into fibrillæ, the main microscopical basis of the wool fibre: this fibrillar bundle is surrounded by the layer of scales whose points seen edgewise are the familiar "serrations," another unique feature of wool. The fibres in the fleece form rough irregular helices and are wavy or crimpled along their length. Their dimensions may vary from 1 to 10 in. in length, and from $\frac{1}{300}$ to $\frac{1}{2000}$ in. in diameter, very approximately. In the broad physical aspect, wool is a mass of filaments and it is also a typical colloid, showing marked swelling property in water and chemical solutions together with the special elasticity phenomena characteristic of colloid substances. To these particular chemical and physical features the special technical operations applied in spinning, weaving, dyeing and finishing must be adapted.

Subsequent to certain preliminary work such as mending, burling, perching, etc., the finishing routines on piece goods may be classified into wet and dry processes:

Wet Operations.—Crabbing or greasy blowing; scouring; piece carbonising; milling in soap, acid or "in the grease"; boiling or potting; piece dyeing or bleaching; mechanical drying, *e.g.* by mangle or centrifuge; heat drying, *e.g.* tentering, waterproofing, weighting, shrinking.

DRY OPERATIONS.—Brushing; steaming; dewing or dampening; cutting (shearing), plain or fancy; blowing (steam decatising); raising (wet or dry); napping; pressing.

In general, the wet precede the dry processes and of the former the principal is *scouring*. Even where, as in the worsted side of the industry, the raw wool has received preliminary washing treatments, it is almost invariably necessary to subject the woven pieces to further cleansing: particularly is this required where fabrics will be dyed in piece form. This piece scouring is mainly required because in the manufacture of the yarns, lubricants—olive oil, oleines, etc.—are used: the removal of these is the chief object of scouring. Most washing processes depend on the production of an *emulsion* in the scouring liquor in which the dirt or extraneous matter is dispersed until, when the contamination is completely detached from the textile and suspended in the scouring medium, this latter is then diluted by fresh liquid and drained away. These broad outlines of the washing processes are affected and indeed governed by many chemical and physical factors. Obviously a neutral wool-lubricant like olive oil behaves differently from a crude fatty acid such as *oleine*: the former requires a typical emulsification while the latter may have a direct first application of alkali (soda ash), the so-called saponification scour. Generally, all scours depend on a complex of physical factors, *e.g.* surface tension, viscosity, temperature, adsorption, etc. The first stage is essentially a *dispersion* in which wetting-out by an agent capable of lowering surface tension is effected. Next this is stabilised by the formation of *adsorption* layers on the dispersed particles, a stage in which *interfacial tension* plays an important part. Following this, the dilution by fresh liquid carries away the dirt, leaving a clean fabric. Thus a scouring liquor is usually of a composite character:

(1) Coarse suspensoid, in respect of floating flock or dust particles.
(2) Colloidal emulsion, with regard to the soap and dispersed oil.
(3) Molecular dispersoid, or true solution, with reference to dissolved alkali, etc.

It is obvious that the emulsifying agent is of primary importance. The time-honoured *soaps*, alkali salts of the fatty acids, fulfil this role in large measure, but modern research has introduced many alternatives, generally long chain compounds, sulphonated oils, etc. Many of these are of proved efficiency, but all are more costly in practice. It is possible that special research into the adsorption phenomena of the scouring emulsion will lead to further progress in this universal and fundamental operation.

Setting or Fixing Processes.—Finishing operations are mainly carried out on textures and therefore the effects of the spinning and weaving stages being inherent in the fabrics require attention. Certain distortions arise which must be corrected in order to obtain final cloths completely regular in structure and appearance and for these **crabbing, blowing, boiling,** etc., are applied: the general term *decatising* is sometimes used. In these operations liquid or vapour (hot water or steam) is applied to the wool substance and it is therefore necessary to consider its reaction to this treatment. Wool fibre in its ordinary state is a highly elastic substance, its tensile strength, for example, being equal to that of the weaker metals, silver, copper, etc. But in water at ordinary temperatures, during many hours, the colloid wool will increase its water content from say the average of 16% to over 30%; this swelling is of course accompanied by diminution of elasticity or increased plasticity. This state can be rapidly brought about by increase of temperature. Near the temperature 212°F. the wool substance loses its elasticity, assuming the *plastic state*; if it is then under any mechanical constraint, the form and dimensions then obtaining will be preserved on cooling and drying out. The play of factors here outlined is the basis of producing what is technically known as *permanent set*. A fabric carrying within it all the strains and distortions of high twist in spinning and close setting in the weaving shows at that stage irregularities such as cockling and puckering, wavy and crooked run of twills and checks in patterns, and irregular shrinkages in finishing operations and subsequent wear. A hot water treatment by crabbing, or by blowing in steam, with the fabric in roll form under slight tension, removes these defects owing to the yield of the fibres in the plastic state: the improvement in appearance, flatness, parallelism of twills and weave elements, etc., is very marked.

Shrinking Processes.—The use of water in both liquid and vapour (steam) phases in the setting operations illustrates its extreme importance as an element in the wool colloid. From the average " regain " of 15–16%, wool may drop to about 5% on the one hand and be saturated on the other to over 30%. The outstanding 5% is chemically united to the wool substance and its removal causes permanent decomposition. Above that amount the water content is replaceable and varies with the relative humidity of the atmosphere eventually reaching a maximum approximating adsorption direct from the liquid phase itself. These changes of regain are accompanied by variation in the physical properties, alterations in elasticity and changes in dimensions. The fully swollen wool fibre is about 16% greater in diameter and one-third in volume, but only a few per cents. in length. Both tensional and torsional elasticity diminish greatly. The effects of these changes in a spun and woven texture are to cause corresponding changes which may be summed up as *relaxation-shrinkage*; concurrent changes result in fibre movements in the structure which form new intersections and entanglements in the mass, similarly termed *felting-shrinkage*. It is desirable to prevent these in the wear of the finished garment and to this end special processes are employed in the finishing routine. One of the oldest, based on alternate wetting and drying without constraint, is *London shrinking*. Others employ chemical means such as the application of chlorine as from chloride of lime, in the earlier forms, later as chlorine water (Schofield, " The Finishing of Wool Goods," 1914), and recently in a special evacuated receiver as chlorine gas (Wool Ind. Res. Assoc., B.P. 417719). A novel shrinking process uses sulphuryl chloride (Hall, Hosiery Times, 1937, **11**, No. 99, 22, 25).

The Milling, Fulling or Felting of Wool.—This characteristic phenomenon is the foundation of many finishing methods applied to wool goods and its rationale is still a matter of acute controversy. The terms milling and fulling are properly names of operations, the word "felting" being really descriptive of the interlacing or entanglement of wool fibres which is the essential feature. Actually, "felts" may be composed of other filaments, and in practice structures mainly compounded of fibres other than wool—for example jute—are so described. But the wool fibre felts so readily and produces masses of so much greater density and elastic strength, that it is necessary to discuss the special factors responsible for this. Youatt's century-old speculation that the scales, by their projecting edges, caused an interlocking, leading to felting, can hardly be accepted to-day, but variations ascribing special "fibre travel" effects to this feature are still put forward. It must not be forgotten that the wool fibre has at least half a dozen unique features: spirality, crimpiness, scale structure, exceptional elastic strength, high swelling property, etc., all of which enter into and facilitate the formation of felted masses.

Any type of mechanical stress—tensile, bending, torsion and, in particular, compression will lead to the entanglement of filaments: in practice, impact compression is used in the older stocks, and rolling pressure in the more generally used roller milling machine. Felting stresses in practice produce a porosity in the fabric—ratio of wool substance to total volume—of the order of approximately one-third as a maximum; torsional stresses in yarn manufacture exceed this, attaining more nearly one-half. Practical milling operations are carried out in acid or alkaline solutions or in soap, the essential factor apparently being the marked swelling of the wool tissue; the loss of rigidity then permitting mechanical strains without breakage. On drying out, the elastic properties of the normal wool colloid are regained. All these considerations point directly to the mechanical factor as the primary basis of felting, and felting should be studied with masses of wool, where the phenomenon is exhibited in a typical form and the complications added by spinning and weaving are absent. In technical practice the progress and extent of the milling operation are measured by shrinkage, usually width shrinkage; this is sufficient for practical purposes but is fallacious as a research method. The felting action could be—and in many cases is—marked by the relaxation shrinkages due to the release of strains from the spinning and weaving operations. It is therefore evident that future progress in cloth milling must come from the mechanical side. At present, pieces are milled either individually or in small numbers: the operation is in practice discontinuous and involves much tedious and costly hand-work. But it is essential, both in itself and as a basis for raised and other finishes, especially on the woollen side of the industry.

Other Mechanical Processes.—The principal of these are (i) Shearing, (ii) Raising, (iii) Pressing.

(i) **Shearing, Cutting or Cropping.**—This is the most purely mechanical of the finishing operations and being conducted on the dry cloth involves neither physical nor chemical principles. Judged from an engineering standpoint, the machinery is the most accurate of all finishing plant: cutting machines may be adjusted to a few hundredths of an inch. All the wet operations performed on wool fabrics disentangle loose fibres and, particularly on worsted goods, these must be removed. All degrees of "clear finish" are carried out in practice. Modern shearing plant tends to the use of multiple machines, as many as six blades being fitted into one machine but the three-blade type is perhaps the most generally useful. Certain modifications in the bed, blade, etc., enable fancy patterns, *e.g.* geometrical and floral effects, to be produced by local removal or retention of the pile; such materials, which have an occasional or recurring vogue, are known as imitation Jacquards, fancy velours, etc.

(ii) **The Raising Process.**—This is historically one of the oldest of finishing operations. Following upon a fulling operation effected by trampling the cloth, it was practised in Roman times by the use of the familiar teazle. This traditional appliance is still employed for certain special finishes, *e.g.* the dress-face pile upon billiard cloths, etc. But the bulk of modern raising is performed by raising plant of the wire card type, developed in a practical form in the eighties by Grosselin; this method permits of more powerful action with much increased output. Raising is one of the characteristic operations on wool materials: the fluffy nap, pile or cover associated with woollen fabrics is one of the chief factors in the non-conducting warmth-promoting properties of such goods.

(iii) **The Pressing Process.**—This is practised on wool fabrics for reasons almost entirely æsthetic, very few changes resulting in physical or mechanical properties. In either static or dynamical forms, it nearly always employs the hydraulic principle. If considerations of output demand, then pressing by rollers—the equivalent of calendering in the cotton industry—is employed. But the general predominance of raised or pile finishes in the wool industry precludes a too extensive use of pressing. The older manual operations displayed in the fixed hydraulic paper press are now very largely superseded. Automatic papering and feeding, electric heating, full-width pressing and many other recent improvements have displaced the hand-worker.

Humidity in Wool Goods. Finishing.—The colloid properties of the wool fibre are fundamental in its practical utilisation. In addition to the wet treatment already described most finishing processes involve the special moisture relations of wool substance. Following on the scouring and milling operations, it is necessary to dry the fabric under definite conditions of width and length. This is effected by two processes:—

(1) **Tentering.**—In the special case of blankets the old system of drying "in the fields"

is still carried out, but the demands of modern output have made machine drying universal. The earliest tentering machines date from about 1870, but only in the past twenty years has much improvement resulted, particularly in heat consumption. Older machines consumed 4–5 lb. of steam for each pound of water evaporated from the cloth; modern plant works with a consumption of less than 2 lb. of steam. It is only in recent years that the enormous cost of generating the high latent heat (966 B.Th.U.) of evaporation of water seems to have been fully realised in the textile trade. Mechanically the modern tenter has advanced greatly by the provision of variable speed gears, automatic feeds, etc., also improvements have been made on the thermal side. The non-conducting or thermal insulation of the machine is to-day essential for the stoppage of high radiation losses. Better utilisation of the moisture-carrying power of the heated air is effected by re-circulation in whole or in part, and for the most rapid and complete evaporation of cloth water, the drying air must be sent through the cloth rather than merely over its surfaces. The physical principles governing evaporation by air currents are now better understood; air power is increased and higher velocities in the air flow are applied, and, as a general result, the modern tenter has double the efficiency of the older types.

(2) Steaming and Dampening Processes.—These processes, the converse of the drying operations, add moisture to the wool fibre. It has been previously stated that the elastic properties are largely controlled by the state of humidity: the characteristic " handle " of wool material—a happy combination of springiness with softness, etc., depends mainly on the percentage humidity (" regain "). As some processes, *e.g.* tentering. blowing, etc., alter this humidity materially, moisture is added to the fibre either by steaming, dewing or dampening as a spray, or even in special operations such as London Shrinking. Steaming from an open trough at atmospheric pressure is a rapid method of humidifying the wool tissue and is widely adopted where output is desired. Humidification by a spray of water droplets,—fine jets playing on to an oblique glass surface—gives better results on the cloth, but in this latter case, ample time should be allowed for diffusion of the moisture from the surface to the interior of the fibre; this factor, a matter of several hours, has not been too well understood in the industry.

General Considerations.—It will be seen from the foregoing matter that to-day some degree of theoretical guidance in the technics of wool finishing is possible. It is essentially an art dependent mainly on physical and mechanical principles with some guidance from wool chemistry. The appliances and machinery of the art have received much improvement in the last 20 years. Indeed, in some cases, *e.g.* shearing machines, it is difficult to foresee possible improvements, and in others, milling or fulling plant, little change has been made for many years. Progress in organic chemistry—particularly in the chemistry of the proteins—has yielded much knowledge of wool keratin, *v.* Fibres, Animal, Wool and Related Fibres (this Vol., p. 98).

J. S.

FINNEMANITE.—Chloro-arsenite of lead, $3Pb_3(AsO_3)_2 \cdot PbCl_2$, found in hæmatite at Långban, Sweden, as black hexagonal prisms, resembling mimetite, but differing from this in being a chloro-arsenite rather than a chloro-arsenate (G. Aminoff, Geol. För. Förh. Stockholm, 1923, **45**, 160).

L. J. S.

FIRE-CLAY. A refractory clay suitable for the manufacture of fire-bricks for furnace-linings, gas-retorts, crucibles, glass-house pots, etc. The qualities required for such goods are that they should retain their size and shape during firing, possess strength and durability, resist high and sudden changes of temperature, and the corrosive action of hot liquids and gases. The attainment of a combination of these qualities best suited to any particular purpose will depend more on the physical characters of the fire-clay than on its chemical composition, and actual trial of samples is desirable rather than detailed analyses. It is, however, essential that the material should consist mainly of aluminium silicate, with only small amounts of alkalis, calcium, iron (especially as pyrites), and titanium, all of which have the effect of lowering the fusibility. The presence of free silica also has the same effect, but to a much less degree. Pure kaolinite $H_4Al_2Si_2O_8$, m.p. about 1820°, and quartz m.p. 1710°, as cristobalite (*q.v.*) are both highly refractory, but mixtures have a lower melting-point than either, with a minimum of 1630° for 90% kaolinite and 10% quartz. This is, however, still above the lower limit (about 1600°) usually allowed for a fire-clay. The best fire-clays occurring beneath beds of coal in the English coal-measures contain Al_2O_3, 20–30% and SiO_2, 50–70% (corresponding to about 3–23% of free silica). With increasing amount of silica these clays gradually pass into sandstones, which are also used as refractory materials; *e.g.* ganister (*q.v.*) and the so-called Dinas " clay " from the Vale of Neath in Glamorganshire, containing as much as 98% of silica. The following analyses are of fire-clays from: I. Stourbridge in Worcestershire, by C. Tookey (*also* P_2O_5, 0·06%). II. Dowlais in Glamorganshire, by E. Riley. III. Betterbed fire-clay from Bowling in Yorkshire, by J. W. Westmorland (*also* TiO_2, 0·87%). IV. Plastic fire-clay from St. Louis, Missouri,

	I.	II.	III.	IV.
SiO_2	65·10	67·12	68·12	57·62
Al_2O_3 . . .	22·22	21·18	26·69	24·00
Fe_2O_3 . . .	—	1·85	2·00	1·9
FeO	1·92	—	—	1·2
MgO	0·18	0·84	0·59	0·3
CaO	0·14	0·32	1·15	0·7
Na_2O	—	—	—	0·2
K_2O	0·18	2·02	1·17	0·5
H_2O	7·10	4·82	0·20	10·5
Moisture . . .	2·18	1·39	—	2·7
Organic matter .	0·58	0·90	—	—
	99·60	100·44	99·92	99·97

quoted by H. Ries, 1908 (*also* SO_3, 0·35%). (For a large series of analyses of British and foreign fire-clays, *v.* Percy's Metallurgy: Fuel, 1875, 87.)

The celebrated fire-clay of Stourbridge in Worcestershire is remarkable for the small amount of contraction that it undergoes when fired, the shrinkage of the unrefined clay being in some cases as low as 1%. For the purpose of reducing shrinkage, fire-clay is often mixed with 'grog,' *i.e.* burnt fire-clay, which has also the effect of giving sufficient porosity to the fire-bricks to enable them to withstand sudden changes of temperature. A greater degree of porosity, with correspondingly less strength, required in the fire-bricks of household stoves, is often produced by mixing sawdust with the clay.

A fire-clay occurring in the Millstone Grit series at Glenboig in Lanarkshire, has been examined by J. W. Gregory and D. P. McDonald (Proc. Roy. Soc. Edin. 1910, **30**, 348, 374), who find that the fine-grained clay substance forming the bulk of the material is present as minute rounded granules about 0·001 mm. in diameter; this is amorphous and not crystalline, and is referable to the mineral species halloysite rather than to kaolinite. Embedded in it are abundant grains of quartz, some grains of felspar, and minute crystals of a rhombohedral carbonate referred to sideroplesite (a variety of chalybite). A bauxitic clay from Kilwinning, Ayrshire, contains boehmite and diaspore (J. de Lapparent, Bull. Soc. Franç. Min. 1935, **58**, 246; Sum. Progr. Geol. Survey, Great Britain, for 1934, 1936, pt. 2, 1).

Bibliography.—H. Ries, "Clays, their Occurrence, Properties, and Uses," 3rd ed. New York, 1927; A. B. Searle, "Chemistry and Physics of Clays" 2nd ed. London, 1933; A. B. Searle, "Refractory Materials," 3rd ed. London, 1940.

L. J. S.

FIRE EXTINCTION AND PREVENTION.—Combustion, as it exists in ordinary cases of fire, is due to the rapid combination of the burning material with the oxygen of the air at temperatures above the ignition-point. It may be extinguished either by lowering the temperature of the burning mass below the point necessary for the continuance of the combustion, or by cutting off the access of air, and so depriving the combustion of the oxygen which is essential for its support.

The usual method adopted for extinguishing a fire is to pour on to the blazing material a large volume of water, and this acts partly by rendering heat latent in its evaporation, and so cooling down the burning mass, and partly by the steam generated driving back the air and so giving time for the cooling action to take effect.

The force with which the water is thrown upon the burning body also produces a considerable effect by sweeping the flame from the surface and so extinguishing the burning gaseous products.

Although, in round figures, 1 lb. of well-dried wood on combustion will convert about 5 lb. of water into steam, yet in the early stages of a fire it is only the surface of the wood that is burning, so that the 5 lb. of water will have a useful effect over a considerable surface, whilst the steam generated occupies a volume about 1,700 times that of the water used.

In the use of water, a certain amount of discretion is necessary, as otherwise undesired results may follow. For instance, in a big warehouse fire, the lower portion soon becomes a mass of red-hot carbonaceous matter, and if water is recklessly played into this, the water is almost instantly turned into steam, which is decomposed in passing through the surrounding red-hot carbon, forming a mixture of hydrogen and carbon monoxide, known as "water gas." This gas is inflammable, and by its combustion adds to the general blaze, while, if it escapes being ignited, it may collect under ceilings and roofs, where, mixing with air, it forms a highly explosive mixture liable to be ignited by any chance flame or spark.

If, however, the water is directed on to the top of the mass, the carbonaceous matter is cooled downwards, so that the steam evolved does not pass through the glowing carbon, and there is thus the minimum generation of inflammable products.

The supply of water necessary for fire extinguishing is usually derived from hydrants, fixed to street mains, which also supply water for domestic, sanitary, and manufacturing purposes.

A sufficient pressure is usually available from such sources of supply as to enable jets of water, distributed through flexible hose pipes, to reach to the seat of the fire.

Where such pressure is inadequate, it is augmented by portable pumping apparatus forming part of the equipment of fire brigades.

No system of fire protection can be considered adequate that does not ensure a constant supply of water under pressure at all hours of the day and night.

Automatic fire protection for the interior of buildings can be secured by the provision of a series of sprinklers suitably situated and attached to a pressure-water piping system. The orifices of the sprinklers are closed by a sealing device secured by a metal fusible at a temperature approximately 155°F. As soon as such a temperature arises due to the heat of conflagration the sealing device collapses and water is distributed over the area desired.

The increasing use of oil products throughout the world calls for entirely special methods of extinction suited to the heavy risks involved.

It has been found possible to extinguish burning oil, by bombarding the burning surface with water under pressure in a finely divided state, the particles of water in contact with the burning material forming a temporary but incombustible emulsion. Petrol, however, cannot be dealt with successfully in this manner.

The practice most generally adopted for the protection of oil and petrol storage tanks is the application of a foaming substance containing carbonic acid gas, to the surface of the oil. The first reference to such a substance amongst English patent records is that contained in B.P. 18357 of 1906 to A. G. Laurent of Petrograd.

Foam of a suitable nature for the purpose required is obtained by mixing saturated solutions of bicarbonate of soda and aluminium sulphate with a stabiliser, which may be of a variety of substances such as saponin, glue, liquorice powder or quassia bark. The two solutions are used in the most convenient proportions for the mechanical methods of their application. The solutions when mixed produce foam in a bulk of approximately ten times their volume, containing in its mass CO_2 gas in large quantities, and of a nature to flow readily over a burning surface, and substantial enough to withstand rapid disintegration. Foam to an even depth of 6 in. over the burning material is considered sufficient for extinction.

The solutions can be stored in tanks of a sufficient capacity to provide enough foam for the risk involved, or they can be made as required in small tanks having a continuous and controlled water supply into which the dry ingredients are introduced by mechanical means at a desired rate. In either system a pumping apparatus is usually employed delivering the two liquids through separate pipe lines to the point where foam is required. When comparatively small quantities of foam are needed such as for the protection of ships' engine and boiler compartments, the solutions can be supplied by gravity from tanks situated on an upper deck, or by steam or air pressure from closed solution-tanks.

Another method for the continuous generation of foam, where a high-pressure water supply exists, is to insert the ingredients in the form of a single dry powder, through an open top hopper into a chamber in which a partial vacuum is formed by the passage of water through a nozzle on the injector principle. The water supply enters at one end of the chamber and carries the powder from the opposite end into a pipe line in which the foam is formed.

Two machines of this character can be used to convey two separate powders to a distant meeting-point where foam is formed.

In forcing foam through a pipe of comparatively small diameter under pressure, there is a tendency for the foam to break down and liquefy; therefore it is desirable when pipe lines of any appreciable length are employed, that solutions should be forced through separate lines of pipes to mix at the point of efflux.

Foam cannot be delivered under pressure effectively through a nozzle to the same distance and with the same force as a jet of water, and the ideal conditions to be aimed at are its formation as close as possible to the point of application on the burning liquid and its delivery without undue disturbance of the surface.

Portable foam appliances for garage and general industrial uses are made in liquid capacities varying from 1 gallon to 60 gallons, in which the two solutions are carried separately in a container, and which on being brought into contact react chemically to generate carbonic acid gas at sufficient pressure to expel the resulting foam through a short pipe line and distributing nozzle.

Apparatus for the continuous generation of foam for city fire brigade use can be readily accommodated on an automobile vehicle, the water supply being obtained from street hydrants, and the pumping apparatus operated from the transmission gear of the automobile.

A successful method for the production of foam in conjunction with a petrol automobile fire-appliance is to utilise the exhaust gases from the petrol motor, which contain a large percentage of CO_2, and to introduce them through a special mixing chamber into a stream of water under pressure from a street hydrant. A quantity of foam-producing compound is also forced into the mixing chamber by means of a small pressure pump operated from the lighting circuit of the automobile. An entirely efficient foam is thus made and delivered through an ordinary length of fire hose and nozzle.

The same result can be obtained by the substitution of compressed air for exhaust gas, the air in most cases being compressed by the same source of power that provides the necessary high-pressure water supply.

Air foam can also be made and distributed through a nozzle by the formation of a partial vacuum at the base of the nozzle, by means of a pressure water supply on the injector principle, drawing in a sufficient supply of air at atmospheric pressure and a liquid stabiliser from a separate source of supply.

Carbon tetrachloride is an efficient extinguisher for fires of a largely varying nature, and for those caused by defective electric insulation. It can be safely used in the presence of high voltage currents, where it would be dangerous to apply either water or foam.

The most common form of apparatus for the distribution of carbon tetrachloride is a hand-worked piston pump fitted into a cylindrical container. Standard appliances are available, varying in capacity from 1 pint to several gallons. Carbon tetrachloride can also be stored in a closed receptacle and discharged therefrom by pressure of carbon dioxide released by means of a perforated capsule.

Carbon tetrachloride is found also to be a most convenient fire extinguisher for fires on automobiles, caused by the combustion of petrol. On reaching the burning material the liquid is instantly vaporised, forming a heavy black pungent smoke and having a blanketing effect by the exclusion of oxygen.

Methyl bromide is a fire extinguisher, having special characteristics which make it convenient for use in aeroplanes. It is usually carried in hermetically sealed vessels under constant pressure, and released by the destruction of the sealing device.

Care should be taken in the use of carbon tetrachloride and methyl bromide as fire extinguishers in enclosed spaces, as irritant and toxic conditions may obtain, requiring thorough ventilation subsequent to their employment.

Liquid carbon dioxide is largely employed for the protection of electric generating stations and the cargo spaces of ships. It is anhydrous, a non-conductor of electric current, and can be effectively employed where the application of water would be dangerous or deleterious to the material to which it is applied.

Liquid carbon dioxide is stored in steel cylinders having capacities up to 100 lb. weight. Such a quantity when expanded into the atmosphere represents approximately 900 cu. ft. of gas at atmospheric pressure. As many cylinders can be employed as the cubic capacity of the fire-risk area necessitates.

Normal air when diluted with approximately 25–30% of carbon dioxide at atmospheric pressure will not support combustion, and under the regulations laid down by the International Convention for the Safety of Life at Sea, 1929, such concentration is called for in connection with the fire protection of cargo spaces of passenger-carrying ships. For these purposes the gas should be released from its storage cylinders as quickly as possible, and the orifices of the cylinders and the piping leading therefrom should be so proportioned as to allow of this result being obtained without any tendency for such orifices to become obstructed by frozen particles through the rapid expansion of the gas from its liquid state.

To secure rapid distribution a variety of methods are in practice for the control of the cylinder valves, either at close quarters or from a distance. The method most generally in use is the perforation of a metal disc closing the valve orifice either through a hand or mechanically operated lever. Distant and automatic control of distribution can be obtained by thermostat devices.

A carbon dioxide equipment is usually carried on automobile apparatus, for use in aerodromes to deal with fires on crashed aircraft or in the hangars. By the instant release of a sufficient quantity of gas distributed through a flexible hose pipe it has been found possible temporarily to produce such conditions in the area of the flaming plane as to allow the approach of a rescue squad to release personnel in jeopardy.

Carbon dioxide fire extinguishers are made in a variety of portable forms having cylinders up to 12 lb. capacity for manual use, or with cylinders of capacities up to 40 lb. for fixing on wheeled appliances. Such appliances are extremely useful in dealing with small fires in enclosed spaces, especially those involving burning oil with a surface combustion and those caused by defective insulation of electric currents.

What is generally known as the "Chemical Extinguisher" is largely used for dealing with fire in its earliest stage. It consists of a metal cylinder of a capacity approximating to 2 gallons containing a solution of sodium bicarbonate in water and an hermetically sealed glass tube containing sulphuric acid of a specific gravity 1·8.

Through the fracture of the tube by internal means a chemical reaction is obtained, by which CO_2 gas at a sufficient pressure ejects the contents of the cylinder through a distributing nozzle.

The CO_2 gas is rapidly dissipated into the atmosphere and has little or no effect on the fire, the value of the appliance being a ready source of water supply under pressure.

By the substitution of a solution of aluminium sulphate for sulphuric acid and the addition of a stabiliser to the soda solution the chemical extinguisher can be made to generate foam. A chemical extinguisher to meet official requirements should be constructed in accordance with the specification of the British Standards Institute.

A pail of water with a hand-operated pump for its distribution over the area involved has been found in practice to be the simplest and most effective appliance for extinguishing fire in its earliest stages.

The most complete handbook dealing with the above subject is the "Crosby-Fiske-Forster Hand Book of Fire Protection," published by the National Fire Protection Association, Boston, U.S.A.

J. H. O.

FIREPROOFING OF FABRICS.

The term "fireproofing" as applied to fabrics is not used in the dictionary sense. It implies a treatment with suitable deposits which render the fabric incapable of propagating flame. Such a fabric chars when brought into contact with an igniting source, and the gaseous decomposition products thus generated may burn on the surface, but flame is not propagated beyond the charred area. Fireproofing may thus reduce fire risks very considerably since the fabric does not then assist in the spreading of flame.

A treatment which prevents flame propagation may not necessarily prevent smouldering or afterglow of fabric. This may persist after the igniting flame has been removed and the whole of the fabric may be destroyed by flameless combustion. The greatest degree of safety from fire risks is therefore obtained by using a process which, besides preventing flame propagation, also prevents afterglow, or in other words, possesses both fireproofing and glowproofing properties.

Although a wide variety of fireproofing treatments are known, employing single substances or mixtures of various degrees of complexity, they may be classified into two types: the Temporary or Soluble Type which is removed by contact with water, and the Permanent or Insoluble Type which is intended for use on fabrics which are to be exposed in the open or are required to retain their fireproofness after washing.

Relative inflammability of textile materials.—A strip of untreated cotton fabric suspended vertically and ignited at its lower edge burns with increasing rapidity until the whole strip is consumed. After the passage of the flame a black mass still possessing the fabric structure is left, which glows at the edges. The glow gradually travels across the strip leaving a black gossamer ribbon containing only a trace of carbonaceous matter. The rate of flame propagation depends on the width of the strip and on the weight and closeness of weave of the material.

A strip of 4 oz./sq. yd. aero cotton 3 ft. long and 6 in. wide, when ignited at its lower edge, burns the last 2 ft. at the mean rate of about 1 ft. in 4 seconds.

Linen, hemp and jute fabrics behave similarly to cotton, but the rate of flame propagation is slower.

Rayon fabrics may be regarded as having approximately the same inflammability as cotton, the acetate being the least inflammable.

Woollen fabric on the application of flame, first chars and then melts, giving off volatile matter which burns, and this melts a further portion. After a short length has burned the molten mass becomes detached, carrying the flame with it, and the strip ceases to burn. The detached mass burns for a few seconds only and does not glow.

Silk fabric chars and melts at a lower temperature than woollen fabric, giving a much less viscous mass, which soon becomes detached carrying the flame with it and the strip ceases to burn; a hard, glossy ash is left which does not glow. This behaviour of woollen and silk fabrics when ignited makes them sufficiently fire-resisting for most purposes.

Fireproofing processes have generally been developed in the first place for cotton fabrics, since the fire risks, especially in relation to this material, are regarded as constituting a serious drawback to its use for many purposes. The results obtained with cotton may be expected to apply to material composed of vegetable fibres, such as linen, hemp, jute and, to a limited extent, to rayon fabrics.

Evaluation of fireproofness.—In evaluating the fireproofness of fabric which has been impregnated with deposits with the object of preventing flame propagation, the specimen under test may be fixed vertically, horizontally or obliquely. In one method the material is hung by an edge from a wooden lath and a lighted taper is applied at the middle of the bottom edge. If less than 5% of the total area is consumed at the end of 1 minute the material is described as fireproof.

With the fabric in a horizontal or oblique plane, the tip of a standard flame is allowed to play on the underside for a stated time. In some cases a hole is made in the centre of the specimen and a flame brought to bear on the edge of the hole. The degree of fireproofness is assessed from the amount of fabric destroyed.

There is little doubt that the vertical strip method provides a more severe test for fireproofness than the other methods and probably gives more concordant results. One method which has been used, is carried out as follows[1]:—The material is cut into strips 18 in. long and 1 in. wide. The strips are suspended vertically in a box perforated at the top and bottom and provided with a glass door. A flame 1 in. long from an orifice 0·5 mm. in diameter is introduced through a hole in the side of the box, allowed to play over the whole of the lower edge of the strip for 10 seconds and then removed. If not more than a 3-in. length of the specimen is charred the fabric is regarded as fireproof.

When the igniting source is removed the charred mass may glow at the edges and the glow may extend over the whole of the charred area and sometimes beyond it. The fabric is regarded as glowproof if the glow does not travel more than a length of 1 in. beyond the original charred area.

Besides preventing propagation of flame and the afterglow effect, a fireproofing process should not deteriorate the strength of the fabric or promote the growth of micro-organisms or be of a poisonous nature. It is also important in many cases that the flexibility of the fabric be retained. For use on fabrics which have to be ironed, a proofing is required which has no deleterious effect under the action of heat.

FIREPROOFING PROCESSES.

Historical.—The records on the fireproofing of fabric date back to 1638. In that year Sabattini[2] published a book dealing with the danger from fires in theatres and recommended that clay and plaster of Paris be mixed with the paint used on the canvas employed for decoration. The first patent dealing with the fireproofing of fabric was granted to Wyld[3] in 1735 for a solution of alum, borax and ferrous sulphate. Alum was also recommended by Poldhelm[4] in 1739, and this substance was used by Montgolfier for impregnating his balloons. In 1786 Arfird[5] suggested the use of ammonium phosphate for fireproofing theatre curtains. The first systematic investigation on fireproofing appears to have been carried out by Gay-Lussac[6] in 1821. He impregnated strips of fabric with solutions of various salts and noted the effect when the material was subjected to a flame. It was concluded that the most active salts were those which had a low melting point and covered the surface of the fabric with a glassy layer or which gave off non-inflammable vapours on heating. Some 40 years later Versmann and Oppenheim[7] examined a large number of salts and classified them in accordance with their fireproofing properties. Under the heading of useful salts were placed sodium tungstate, ammonium phosphate and ammonium sulphate. By about the middle of the nineteenth century most of the soluble salts now recognised as fireproofing agents had been used or suggested for fireproofing, either alone or in mixtures. To assist impregnation of the fabric by the fireproofer, saponin was suggested by Leger.[8] Various methods have been proposed to improve the adhesion and prevent dusting off on handling, of salts which crystallise on fabric; starch and glue have been used for this purpose. A number of mixtures of salts have been described which are stated not to crystallise on fabric.

The possibility that a fireproofing agent may encourage bacterial growth on fabric has been referred to and to prevent this carbolic acid and similar germicides have been added. All the early fireproofing agents were essentially of the Temporary type. The introduction of flannelette as a substitute for wool led to considerable activity in attempts to obtain a fireproofer of the Permanent type which would withstand the normal laundry treatment. In this connection Perkin[9] developed the stannic oxide process and Craig[10] *et al.* put forward a process employing a double carbonate of aluminium and sodium. A method of fireproofing fabric by covering it with a metallic layer was devised by Schoop.[11] Aluminium was used to reduce the inflammability of balloon fabric. In more recent years a number of fireproofing processes have been published which employ organic substances such as chlorinated naphthalenes, halogen substitution products of carbocyclic compounds and alkylamine salts of inorganic acids.[12]

TEMPORARY FIREPROOFERS.

The simplest and cheapest way of fireproofing fabric is to immerse it in an aqueous solution of a suitable soluble salt. The fabric is then wrung out and dried. Many suitable salts are available. Such processes are for use only on fabrics which are not exposed in the open or laundered.

Single Substances.—A classification of a number of soluble substances in accordance with their fireproofing properties has been made and is given below. This is based on the vertical strip method of evaluation detailed above. In this classification substances are described as—

A. Fireproofers and glowproofers.
B. Fireproofers.
C. Non-effectives.

The minimum quantities of the substances in Classes A and B, expressed as percentage weight of the fabric, required to prevent flame propagation of a 4-oz. aero cotton are given. Substances are regarded as non-effectives, Class C, if they do not prevent flame propagation when present in amounts greater than 70% of the weight of the fabric.

CLASSIFICATION OF SOLUBLE DEPOSITS.

A	Wt. %	B	Wt. %	C
Ammonium borate	24	Ammonium vanadate	9	Ammonium alum.
Ammonium bromide	7	Arsenic acid	20	Ammonium carbonate.
Ammonium chloride	22	Lithium hydroxide	5	Ammonium nitrate.
Ammonium iodide	14	Potassium carbonate	16	Ammonium tungstate.
Ammonium molybdate	7	Potassium hydroxide	8	Boric acid.
Ammonium phosphate	12	Potassium nitrate	13	Guanidine carbonate.
Ammonium sulphate	18	Potassium permanganate	22	Lead nitrate.
Borax	60	Potassium phosphate	27	Microcosmic salt.
Calcium chloride	14	Potassium dihydrogen phosphate	30	Potassium alum.
Guanidine phosphate	19	Potassium thiocyanate	25	Potassium hydrogen phosphate.
Magnesium chloride	16	Sodium bicarbonate	23	Potassium ethyl sulphate.
Phosphoric acid	10	Sodium carbonate	12	Sodium chloride.
Sodium aluminate	19	Sodium hydroxide	10	Sodium dihydrogen phosphate.
Sodium arsenate	33	Sodium molybdate	6	Sodium hydrogen phosphate.
Sodium bisulphate	30	Sodium phosphate	20	Sodium sulphate.
Sodium silicate	20	Sodium selenite	36	Sodium thiosulphate.
Sodium stannate	18	Sodium vanadate	2½	
Sodium tungstate	9			
Zinc chloride	12			

Many of the substances in Class A have been and are still extensively used for fireproofing. Ammonium bromide, ammonium sulphate, ammonium phosphate and sodium tungstate may be singled out as fireproofers readily procurable and of high efficiency.

Effect on the Strength of Fabric.—The early observers Versmann and Oppenheim[5] and Keghel[13] found that many substances used for fireproofing had a destructive action on fabric. Sibley [14] boiled pieces of light and heavy duck in solutions of various fireproofers and determined the breaking strength. In most cases considerable tendering occurred, sodium tungstate having the least effect. The results of tests by Ramsbottom and Snoad [1] on the changes in strength of a 4-oz. aero cotton proofed with various substances (1) when kept in a room at ordinary temperatures, (2) exposed to sunlight under glass, and (3) heated to 120°C., are given in the table in the next column.

Deposit.	% Loss in tensile strength.		
	(1)	(2)	(3)
Ammonium borate	No appreciable loss in strength	20	19
Ammonium bromide		91	91
Ammonium chloride		93	94
Ammonium phosphate		49	43
Ammonium sulphate		61	54
Borax		41	51
Calcium chloride		86	17
Sodium silicate		49	4
Sodium tungstate		82	3
(Fabric control)		30	0

(1) Exposed in a room at ordinary temperature and humidity for 300 days.
(2) Exposed under glass at 45° in the open, facing south, for 200 days.
(3) Heated in an oven at 120°C. for 4 hours.

Although at ordinary temperatures no appreciable deterioration occurred with any of the deposits, exposure to sunlight or elevated temperatures caused, in most cases, a considerable loss in strength. From these results it may be concluded that for the fireproofing of curtains and similar materials exposed behind glass to direct sunlight, ammonium borate and borax would probably be least destructive. For clothing and materials which are to be subjected to the laundry ironing process or are to be exposed above ordinary temperatures, sodium tungstate seems to be the obvious choice.

Mixtures.—The majority of fireproofing processes put forward employ mixtures of substances. This is readily understood as it seems likely that the deficiencies of a fireproofer in any particular respect can be overcome by the addition of one or more substances which possess or can impart the desired property. A large number of suitable binary mixtures are available. Mixtures of ammonium salts are frequently used, but as the properties of these mixtures are the sum of the properties of the constituents there is little to be gained by using such mixtures in preference to the single salts.

Mixtures of alkali metal salts may, however, be more effective fireproofers than the constituents.

Although ammonium salts are decomposed by many of the alkali metal salts used for fireproofing, such mixtures are sometimes used. In some cases the fireproofing properties of the constituents are partly destroyed by admixture, but in a few cases improvement results.

A number of binary mixtures containing boric acid possess outstanding properties. Mixtures of borax and boric acid are of special interest. The most effective mixture appears to be one containing 30% boric acid. This mixture, when applied to light cotton fabric to the extent of about 6% of the weight of the fabric, prevents the propagation of flame and afterglow.[1] The proofed fabric retains its softness and flexibility and does not become dusty or feel damp. Specimens stored for 100 days at ordinary temperature retain their strength unimpaired. When stored at 40°C. the loss in strength after 365 days was found to be 7%, and specimens exposed under glass to direct sunlight for 100 days lost 27% of their strength, the untreated fabric losing 20% during the same period. The mixture is non-poisonous and has been shown not to promote the growth of destructive micro-organisms. It is cheap and its application to fabric is simple. There is little doubt that such mixtures owe their efficiency as fireproofers partly to the fact that they do not crystallise on the fabric. A number of ternary mixtures have been proposed which possess advantages over binary mixtures in that their fireproofing efficiency on a weight basis is slightly greater. One successful mixture is borax 50, boric acid 35, sodium phosphate 15. This prevents flame propagation on light cotton with an added weight of 5%. No afterglow occurs. Less improvement can be expected in quaternary mixtures, since theoretically the scope for improvement will become less as the number of the constituents increases. It is probable that none of the quaternary mixtures put forward shows any marked improvement over the best binary and ternary mixtures, particularly as regards flame propagation and afterglow.

PERMANENT FIREPROOFERS.

Water-soluble deposits are not suitable for fabrics which are to be exposed in the open air, and a deposit of the insoluble type is necessary for fireproofing such fabrics as tent and hangar canvas, deck awnings and outdoor covers of various kinds.

The problem of preparing a suitable permanent fireproofer is much more difficult than the production of temporary fireproofers, since a permanent fireproofer may have to withstand prolonged exposure to rain, sunshine and wind. It is generally recognised that no satisfactory permanent fireproofing process has yet been evolved, but a considerable measure of protection against fire risks is possible, especially with respect to flame propagation.

Single Substances.—A classification, as shown in the table on p. 214, of a number of insoluble deposits representing various classes of chemical compounds has been made on the lines of the method given above for soluble substances. The deposits were generally formed from two solutions by double decomposition, but in a few cases a single solution was used which gave an insoluble deposit when the impregnated fabric was dried and then immersed in boiling water. After proofing the specimens were washed in running water for 1 hour.

In this classification the columns show A, fireproofers and glowproofers; B, fireproofers; C, non-effectives. The figures in A and B are the minimum amounts of the deposits necessary to prevent flame propagation, expressed as percentage weight of the fabric, while in C they are the maximum amounts which could be conveniently precipitated on the fabric. Deposits in Class C adhered badly to the fabric in many cases, and the afterglow effect was not generally observed when the burning fabric was extinguished.

Only one of the substances possessed both fireproofing and glowproofing properties and only a few prevented flame propagation. The contrast in behaviour between insoluble and soluble deposits is very striking, as in the latter case 37 out of the 53 substances tested prevented flame propagation. Apart from antimony oxychloride, the most effective fireproofers were ferric oxide, stannic oxide, lead oxide and manganese dioxide.

Effect on the Strength of Fabric and Permanence to Weathering Action.—The results of exposure tests on a 4-oz. cotton fabric proofed with various deposits and exposed at an angle of 45° for 6 months, in the open air, facing south, are given in the table at foot of p. 214. The specimens were also tested for fireproofness.

At the end of the exposure only two of the specimens, those with ferric oxide and lead oxide, prevented flame propagation. Most of the specimens underwent a greater loss in strength than untreated fabric. Stannic oxide and titanium oxide caused complete destruction. Lead chromate, chromic oxide and ferric chromate had no deteriorating action, while silica and alumina gave a measure of protection. Although these latter deposits are not fireproofers, they are useful constituents for mixtures as no afterglow occurs with fabric on which these substances have been precipitated.

There is little doubt that on a weight basis

Classification of Insoluble Deposits.

A	Wt. %	C	Wt. %	C	Wt. %
Antimony oxychloride	30	Aluminium acetate (basic)	140	Ferric phosphate	40
B	Wt. %	Aluminium borate	59	Lead chloride	24
Aluminium stannate	54	Aluminium fluoride	76	Lead peroxide	60
Antimonious oxide	79	Aluminium oxide	70	Magnesium ammonium phosphate	125
Ferric chromate	24	Aluminium silicate	100	Magnesium borate	35
Ferric oxide	19	Aluminium tungstate	60	Magnesium oxide	15
Lead chromate	37	Barium carbonate	91	Magnesium silicate	116
Lead monoxide	21	Barium oxalate	78	Nickel oxide	75
Manganese dioxide	22	Barium sulphate	100	Potassium silicofluoride	64
Stannic oxide	20	Bismuth trioxide	40	Silica	400
Tin tungstate	50	Cadmium oxide	67	Silver oxide	40
Zinc stannate	40	Calcium carbonate	50	Stannous oxide	40
		Calcium fluoride	50	Thorium oxide	60
		Calcium phosphate	52	Tin phosphosilicate	64
		Calcium stannate	46	Titanium oxide	40
		Calcium tungstate	96	Zinc ferrocyanide	48
		Cerium oxide	69	Zinc fluoride	70
		Chromic oxide	91	Zinc oxide	22
		Cobalt oxide	52	Zinc tungstate	54
		Copper oxide	19	Zirconium oxide	120

all the single insoluble deposits are much inferior to the best soluble type. The most effective fireproofer appears to be ferric oxide. It only requires a relatively small added weight to render fabric fireproof, and this property is retained on weathering for at least 12 months in certain cases. Fabric proofed with ferric oxide has, however, the great drawback that when brought into contact with an igniting source it glows and is completely destroyed by flameless combustion.

Treatment of fabric with stannic oxide, sometimes described as Perkin's process,[9] produces a similar effect, but unlike ferric oxide it quickly loses its property of preventing flame propagation when subjected to the action of rain. This property can, however, be restored by treatment of the fabric with dilute alkali. In the ordinary laundry wash, the fireproof condition is retained if the proofed material is only rinsed in water after the soap and soda boil.

Many other deposits, which are otherwise inert, prevent flame propagation when a small amount of an adsorbed alkaline salt is present. Such adsorbed salts are not completely removed by slight washing with water. This explains why many insoluble deposits, such as magnesium borate, aluminium tungstate, other insoluble borates and tungstates as well as phosphates, silicates, hydroxides of aluminium, zirconium, titanium, silicon, zinc and magnesium, have been described as permanent fireproofers. In all cases alkali salts enter into the formation of the deposits and adsorbed salts are retained if the washing is incomplete.

Mixtures.—So far no success has been achieved in attempts to obtain a permanent fireproofing treatment involving the deposition of one insoluble substance only on the fabric. All the effective fireproofers cause vigorous afterglow. To overcome this defect it is necessary to deposit one or more additional substances on the fabric.

A number of binary mixtures have been put forward. Mixtures containing synthetic chlorinated resins have been proposed with the object of preventing afterglow.[16] Inert oxides

Deposit.	% Loss in strength.	Deposit.	% Loss in strength.
Aluminium oxide	10	Ferric chromate	32
Aluminium stannate	90	Ferric oxide	45
Antimony oxychloride	54	Lead chromate	25
Barium carbonate	55	Lead oxide	80
Barium oxalate	52	Manganese dioxide	40
Calcium tungstate	36	Silica	9
Cerium oxide	56	Stannic oxide	100
Chromic oxide	25	Tin tungstate	59
Copper oleate	29	Titanium oxide	100
Copper oxide	33	Zinc stannate	85
		Zinc stearate	43
		(Fabric control)	31

and salts have been tried for the same purpose. None of the binary mixtures so far proposed retain their fireproofing and glowproofing properties sufficiently long to be of practical use for fabrics exposed in the open.

Ternary mixtures containing metallic oxides and waterproofing agents, such as aluminium stearate, have given little improvement over binary mixtures, but some success has been achieved with mixtures of active oxides, such as ferric oxide and stannic oxide, with inert oxides, such as tungstic oxide and silica or with chlorinated compounds.[15] Specimens proofed with some of these mixtures have withstood exposure for 6 months in the open without losing their fireproof and glowproof properties. The main drawback to such processes is the relatively large weight of deposit required which may amount to 1¼ oz. per sq. yd. on a 4-oz. fabric. Also, the process involves a number of precipitations.

Quaternary mixtures based on the same principles as those employed for ternary mixtures have the same defect and the weights involved are correspondingly greater.

It is probable that none of these processes will in practice show a satisfactory behaviour for periods longer than one year.

Mechanism of Fireproofing Action.

Early workers came to the conclusion that the fireproofing action of soluble salts could be explained in one of the following ways: (1) the fireproofing agent fuses below the ignition temperature of fabric and coats it with a layer more or less impermeable to air; (2) the fireproofing agent evolves non-inflammable gases which extinguish flame; (3) the heat of the flame is taken up by some change in the fireproofing agent which absorbs heat; (4) the heat of the flame is dissipated by conduction. Recent investigations [1] have shown that none of these explanations fully accounts for the observed facts. It has been established [1] that the reaction between a fireproofer and cellulose is essentially of a chemical nature. Efficient fireproofing agents act as catalysts attacking cellulose at temperatures below the ignition point and giving rise to volatile products which are not capable of sustaining flame. When fireproofed fabric is brought into contact with flame, charring occurs at the point of contact and in the near neighbourhood, at temperatures below the charring point of untreated fabric, but subsequent flame propagation does not take place.

The afterglow effect which accompanies the use of some deposits which prevent flame propagation is regarded as a secondary phenomenon and is due to the combustion of the carbonaceous matter in the charred fabric, the deposit acting as a catalyst. The action in some cases is sufficiently vigorous to cause the decomposition of unchanged fabric and may lead to its total destruction. Exclusion of air by the formation of a glassy layer or a blanket of inert vapours on the charred fabric will prevent afterglow.

Insoluble fireproofing deposits act as catalysts but with deposits of oxides, the action may be regarded as a catalytic oxidation effect. This explains why only those oxides which are readily reduced prevent flame propagation.

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J. E. R.

FIREPROOFING OF TIMBER.—Owing to its organic nature wood decomposes when exposed to high temperatures. No matter to what treatment it has been subjected it will char, and in presence of sufficient air will be almost entirely consumed. Therefore the term "fireproofed timber" is not strictly accurate. Nevertheless, wood which has been treated with certain chemicals may be subjected to intense heat without flaming and without the fire spreading beyond the heated area; if the source of heat is removed the charred portion rapidly cools without any persistence of burning or glow. It is in this more limited sense that the term is used.

Numerous attempts have been made to introduce a more satisfactory term. Chemicals which confer this property are frequently described as fire retardants, but no more suitable alternative term has yet been coined to describe the process of fireproofing. In British Standard Specification No. 476 (1932) it is recognised that the term "fireproof" is misleading and the following definitions are given for fire-resistance, incombustibility and non-inflammability as applied to building materials and structures:—

> *Fire resistance* is a relative term used in the specification to designate that property by virtue of which an element of a structure, such as a door, beam, or column, as a whole functions satisfactorily for a prescribed period whilst subjected to a prescribed heat influence and load. An *incombustible* material is one which neither burns nor gives off inflammable vapours in sufficien quantity to ignite a pilot flame when heated in the manner specified. Combustible materials shall be graded as "*non-inflammable material*," "*material of very low inflammability*," and "*material of low inflammability*" according to their behaviour when tested in accordance with the specification.

Doors constructed of fireproofed wood are able to resist the passage of fire for 1–2 hours and are therefore classed as fire-resisting. The London Building Act also approves fireproofed wood as fire-resisting; the New York Building Code recognises it as incombustible.

Behaviour of Wood in Fire.

Wood substance, which consists mainly of cellulose, lignin and hemicelluloses, is stable for a reasonable time at temperatures below about 275°C. It is true that at temperatures below 275°C. moisture is removed, and slight decomposition occurs, but this is serious only if exposure is prolonged; wood in contact with hot water pipes darkens and resembles wood which has been decayed by the dry-rot fungus. Campbell and Booth (Biochem. J. 1930, **24**, 641; 1931, **25**, 756) showed that wood exposed to temperatures not exceeding 55°C. for 11 days undergoes sufficient hydrolysis for the effect to be detected by chemical analysis, and incipient hydrolysis of the more resistant softwoods, typified by silver fir, is detectable at 80°C. These chemical effects are accompanied by marked reduction in strength. The importance of careful control of temperatures to suit individual species in kiln-drying is thus evident.

When heated to about 300°C. wood decomposes, inflammable gases and vapours are liberated, and charcoal is formed. If the vapours are liberated in sufficient quantity and ignited the temperature of the adjoining wood is raised, the action spreads rapidly and becomes exothermic; the wood burns. In presence of sufficient air the charcoal glows and is almost completely consumed, only a small amount of ash remaining. The speed of combustion is dependent on the ratio of the surface of the wood to its mass. A small splinter burns rapidly, and the charcoal is readily consumed. A thick baulk of timber becomes coated with a layer of charcoal, and unless more heat is applied, and in the absence of a strong current of air, the charcoal is not consumed but forms an insulating layer on the wood. Heavy timbers are consumed so slowly in large sizes that they retain considerable strength after prolonged exposure in severe fires. This fact is the basis of the " slow-burning heavy-timber " or " mill " type of construction.

Historical.

The problem of fireproofing wood is very old. According to Herodotus, impregnation with alum as a means of fireproofing was practised by the Egyptians. Aeneas Tacticus (400 B.C.) recommended vinegar, and Aulus Gellius reported that the wooden defensive towers at the siege of Piraeus, 87 B.C., were protected from fire by a solution of alum. A British patent on a method for fireproofing the wood, canvas and ropes of ships was issued in 1625. Gay-Lussac (Ann. Chim. Phys. 1821, [ii], **18**, 211) impregnated strips of hemp and linen fabrics with 10 and 20% of various salts and found that mixtures of ammonium phosphate with ammonium chloride or borax (1:1) prevented both flaming and glowing. Versmann and Oppenheim (Brit. Assoc. Reports, 1859, **29**, 87) examined a large number of salts for fireproofing and secondary effects, and classed as useful salts sodium tungstate, ammonium phosphate, sodium ammonium phosphate, ammonium sulphate, and a mixture of ammonium chloride and phosphate. Since that time hundreds of patents have been granted for fireproofing processes.

Fireproofing on a commercial scale appears to have originated in America and was undertaken in response to a demand by the Navy for fireproofed wood for decks and other parts of warships. The process, which was operated by the Electric Fireproofing Company, was that developed by M. Bachert (U.S.P. 502867). The wood was impregnated under pressure with a solution of ammonium sulphate and ammonium phosphate after preliminary steaming and vacuum treatments. Further impetus was given to the development of the industry by the 1899 revision of the New York City Building Code which provided for the use of chemically treated wood for the interior woodwork of buildings over twelve stories high. The Navy discontinued its use in 1902 after experiencing trouble from the corrosion of metal fastenings, and in painting, due to the hygroscopic nature of the fireproofed wood. In 1926 the Bachert process was revived and taken over by the Protexol Corporation of Kenilworth, N.J., which is now the premier fireproofing company in the United States (G. M. Hunt and G. A. Garratt, " Wood Preservation," 1st ed., McGraw-Hill Book Co., New York, 1938, p. 399).

In this country the most important concern is the Timber Fireproofing Company of Market Harborough. The "oxylene" process which they operate employs a solution, patented by A. W. Baxter (B.P. 5209/1905), of ammonium phosphate and boric acid in water, the preferred proportions being 12:1:87. Timber is subjected to steam and vacuum treatment before impregnation (Engineering, 1925, **119**, 11). It is claimed that wood so treated will not ignite or spread fire, that it is not hygroscopic and will not cause corrosion of fittings, that it is resistant to attack by fungus, and that it can be cut or painted as ordinary wood. All wood installed in vessels of the Royal Navy and in the underground rolling stock of the London Passenger Transport Board is fireproofed by this process.

The Mechanism of Fireproofing.

Gay-Lussac was the first to propose a theory of the action of fireproofing salts and his theory has been generally accepted up to the present time. He found that the chemicals act in two ways. Some melt to form a glaze on the surface of the wood and so prevent ingress of oxygen. This is the mode of action of substances such as borax or phosphoric acid. Other substances decompose and liberate inert gases such as water vapour, carbon dioxide or ammonia, which mix with the inflammable gases derived from the wood substance and render them non-inflammable. A salt such as monoammonium phosphate would act in both these ways, and this would account for its high efficiency. Heat would also be absorbed in decomposing the chemical and less heat would therefore be available for spreading the fire; moreover, the higher thermal conductivity of the treated wood would result in increased dissipation of heat.

Gillet (Chim. et Ind., Special No. 1929, 221) showed that if water is present in sufficient quantity the heat required to convert it to vapour could be in excess of that produced by the combustion of the wood when allowance has been made for external loss of heat. Hunt, Truax and Harrison (Proc. Amer. Wood Preservers Assoc. 1932, 71), however, found no consistent relationship between the effectiveness of various chemicals and their water of crystallisation. R. Schlegel, " Unters. ü. d. Grundl. d. Feuerschützes v. Holz. Diss. Verlag Chemie," Berlin, 1934, showed that the extinguishing action of inert gases depends on their average molar heat in the range room-temperature–combustion-temperature, and the effectiveness of the gases examined fell off in the order NH_3, SO_2, CO_2, N_2.

Evidence is now accumulating to show that the effect is mainly chemical, that the action is to dehydrate the wood, *i.e.* to remove chemically combined water, and that the other effects are of secondary importance. N. A. Richardson (J.S.C.I. 1937, **56**, 202T) has shown that wood treated with chemicals known to be effective fire retardants, on carbonisation at temperatures above 300°C., yields considerably more charcoal than untreated wood or wood treated with other chemicals. It was found, too, that the chemicals which have this property, with the possible exception of borax, are those which dissociate on heating to give a free acid radical. Results published by the Forest Products Research Board (Ann. Report for 1938–1939, 40) confirm the view that dehydration is involved (Table I).

TABLE I.—PRODUCTS RESULTING FROM HEATING AT 450°C.

	Untreated wood.	Wood treated with 20% NH_4Cl.
Charcoal	26	48
Condensable organic vapours, tar, etc. . .	33	9
Water	19	35
Uncondensed gases (by difference)	22	8
	100	100

The fire-retardant induces decomposition of the wood substance to carbon and water. This results in a decrease in the amount of inflammable gases and vapours evolved, and these are so diluted that flaming is retarded or prevented.

L. Metz (Holz, 1938, **1**, 217) confirmed the action of acid substances in effecting a premature carbonisation of wood, and suggested that carbonisation is probably preceded by saccharification. He found that alkalis or substances which produce alkalis on heating also accelerate carbonisation, though not to the same extent as acids, but that neutral salts do not. E. F. Hartman (Proc. Amer. Wood Preservers' Assoc. 1935, 218) emphasised the importance of the condition of the charcoal; that from fireproofed wood is very hard and has a large number of fine cracks, whilst that from untreated wood is soft and contains wide, deep grooves.

These theories refer to salts which are used to impregnate wood. On the other hand, fireproof paints and coatings act mechanically in covering the wood with a layer of non-inflammable material and so insulating it from flames or other sources of heat. They do not modify the wood and in large fires often crack and leave the wood unprotected. As many fires start from small sources, however, they are of value in preventing the spread of fire in the initial stages.

Tests for Fireproofed Timber.

Methods of testing the fire-resistance of wood may be grouped broadly into (1) fire-endurance tests for elements of structures in which wood in the form in which it has to be used in buildings (doors, columns, beams, etc.) is tested under conditions which simulate those which occur in a fire; (2) acceptance tests, which set a standard to be attained by fireproofed wood and enable users and plant operatives to tell whether wood is adequately treated. Such tests also enable poor methods to be eliminated; and (3) tests devised to compare the value of different chemicals as fire-retardants.

There are several independent factors involved in the fire-resistance of wood, such as ignition, flame spread, flame penetration, glowing, heat transmission, and loss of strength. Small-scale tests are satisfactory only if they measure at least one of these factors. In the past most workers have devised their own tests and as the units of measurement are arbitrary, there is little correlation between the different results.

Much of the earlier work on the comparison of fire-retardants was carried out on cellulose materials other than wood, such as fabrics and paper with which the ability of flame to spread can easily be observed. In the case of wood the splinter test constitutes a rough qualitative test for fire-retardance. When a splinter of well treated wood is held in a flame it chars, and on removal from the flame any burning or glowing ceases immediately, the charcoal remaining firm and hard. This test cannot be standardised, but developments have led to the more satisfactory shavings, crib and timber tests.

FIRE-ENDURANCE TESTS.—The fire-resistance of structural elements is usually determined by tests on relatively large specimens. Such tests are expensive and can only be carried out in specially equipped testing stations. Stations have, however, been established in various countries, notably Britain, United States, Germany and Sweden. Fire tests on doors were first carried out by the British Fire Prevention Committee of the National Fire Brigades Association in 1899, and results of tests on various structures were published in the Red Books in the succeeding years. In 1935 a station was opened at Elstree by the Fire Offices Committee (Engineering, 1935, **140**, 618) which has facilities for testing fire-resistance in accordance with the British Standards Institution—" Definitions and Methods of Test for Fire Resistance, Incombustibility and Non-Inflammability of Building Materials and Structures " (B.S. No. 476—1932).

British Standard Methods of Test: Fire-Resistance.—Elements of structure are tested. They should be full size or not less than 10 ft. by 10 ft. and restrained or loaded as they would be in service, the test load being 1½ times the design load. Unloaded structures are subjected to a blow from a falling 10 lb. ball, and structures which are fire-resisting for more than 2 hours are also subjected to a water jet.

The surface of the elements is heated to temperatures controlled according to the *standard time-temperature curve, i.e.* to 1,000°F. at 5 minutes, 1,300°F. at 10 minutes, 1,550°F. at 30 minutes, 1,700°F. at 1 hour, 1,850°F. at 2 hours, 2,050°F. at 4 hours, 2,200°F. at 6 hours, and 2,300°F. at 8 hours. The temperature of the unexposed face of walls, floors, etc., functioning as separating structures, must not rise by more than 250°F. above the normal temperature, no cracks should form through which fire might pass, and the structure must remain rigid. According to the length of time during which the elements satisfy the conditions they are classified as Grades A (protection against fire for 6 hours), B (4 hours), C (2 hours), D (1 hour), or E (½ hour).

It should be noted that the test applies primarily to the design of a fire-resisting structure, and not directly to the effectiveness of a fireproofing chemical or a method of fireproofing. Bad design may clearly be the cause of early failure if, for instance, shrinkage cracks form at joints and allow flame to pass.

A test in which a 1¾ in. thick fireproofed wood door successfully withstood a 1-hour test carried out in accordance with the corresponding American Fire Test Specification (A.S.T.M., C. 19–33) is reported in Proc. Amer. Wood Preservers Assoc., 1935, 225. The British Standard Methods of Test are intended for all materials used in building construction. The *incombustibility test* involves heating the material in a vertical electric furnace with a pilot light above and an observation chamber below, the temperature being increased by 900°F. per hour to a maximum of 1,382°F. If the material neither flames nor glows more brightly than the walls of the furnace, or if it glows at all the glow is immediately diminished when the specimen is lowered into the observation chamber, it is incombustible. The *non-inflammability test* which would, however, classify most species of timber as non-inflammable, consists in supporting the specimen at an angle of 45° while 0·3 c.c. of ethyl alcohol is burnt 1 in. below the centre, and noting the duration of flaming and glowing.

New York Building Code Acceptance Tests.—1. *Shavings Test.* A mass of shavings from both inside and outside the sample is placed to form a layer 2 in. thick in a metal vessel 12 in. square, the bottom of which is a wire screen. A yellow Bunsen flame is placed under the vessel for 25 seconds. At no time should the flame show more than 6 in. above the top of the bed of shavings and the shavings should not be consumed in less than 5 minutes. 2. *Crib Test.*—Twenty samples each ½ in. square and 6 in. long are built up on a ring support in five equal tiers making a crib 6 in. square and 2½ in. high, which is set 6 in. above a Bunsen burner. The flame is directed on the crib for 1 minute at a temperature of approximately 1,200°F. The wood must not flame for more than 20 seconds after removal of the burner, nor the glow last for more than 30 seconds. 3. *Timber Test.*—Two samples, each ¾ in. by 1½ in. in cross-section and 12 in. long are laid edge to edge across the top of a gas crucible furnace and exposed for 2 minutes to flame at a temperature of 1,700°F. The samples are removed and the duration of flame and glow is noted. Flame should not persist longer than 15 seconds and glow not longer than 20 seconds. The pieces are then cut through at the most burned section. The unburned areas of hardwoods should be not less than 55% and of softwoods 45% of the original section.

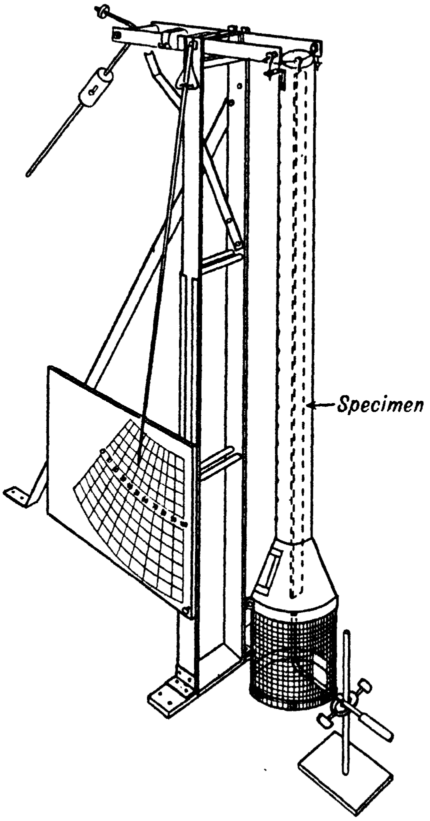


FIG. 1.—U.S. FOREST PRODUCTS LABORATORY FIRE-TUBE.

The shavings test gives a rough indication of resistance to ignition, flaming and glowing, but cannot be standardised. The crib test is valuable in that it gives information on loss of strength, the amount of combustible material present, ignition resistance, and tendency to spread flame. The timber test also is very suitable for measuring combustibility, loss of strength, flame spread and particularly flame penetration (E. F. Hartman, R. C. Bastress, and A. S. Williams: Proc. Amer. Soc. Testing Materials, 1934, **34**, Pt. II, 754).

The timber test is the basis of an A.S.T.M. Specification C. 132–37T, *ibid.* 1937, **37**, 756, " The Fire-Retardant Properties of Wood for Scaffolding and Shoring," and a proposed specification " Fire-Retardant Properties of Wood for Structural Uses " (Proc. Amer. Wood Preservers' Assoc., 1939, 341). In these, 10-in. specimens are used, and the average continuation of flaming must not exceed 30 seconds, nor of glow 30 seconds after cessation of flaming, the average loss in weight being not more than 30%.

Fire-Tube Test.—The most widely used method of measuring flame spread is that devised by the U.S. Forest Products Laboratory (T. R. Traux and C. A. Harrison, Proc. Amer. Soc. Testing Materials, 1929, **29**, Pt. II, 973). The apparatus consists of an open-ended perforated sheet-metal tube in which a specimen ⅜ in. by ¾ in. by 40 in. is burned (Fig. 1).

In carrying out the test the empty tube is balanced by means of counterweights so that the pointer is in a vertical position and reads 100 on the percentage chart. The (weighed) specimen is suspended in the tube and the scale is raised or lowered to bring the end of the pointer on the zero line. A standardised Bunsen flame is placed under the specimen for exactly 4 minutes and then removed. Readings of the percentage loss in weight, as indicated on the chart, and of the temperature at the top of the tube are taken at ¼-minute intervals until 2 minutes after flaming ceases. Typical curves are shown in Fig. 2.

The loss in weight of untreated samples of wood (southern pine) is 80–90% of their air-dried weight (6–7% of moisture), and the maximum temperature reached at the top of the tube is between 700° and 800°C., while well-treated specimens lose about 15–20% of their weight, and the maximum temperatures attained are below 200°C.

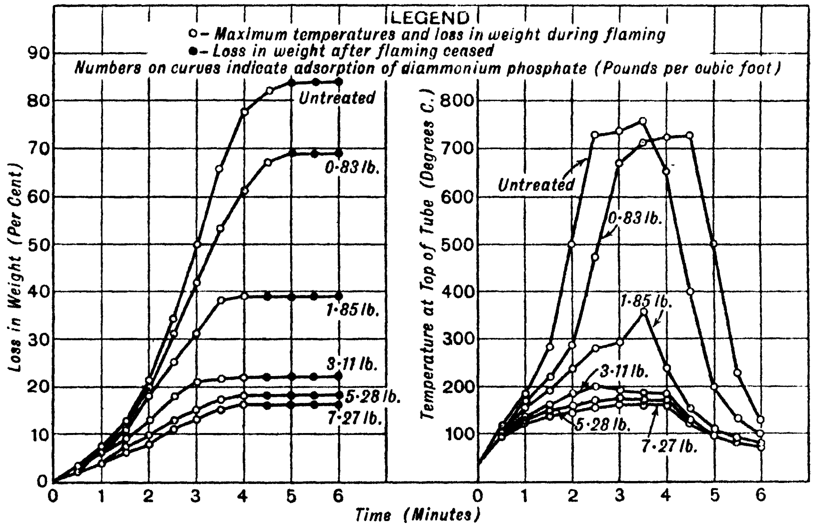


FIG. 2.—TYPICAL CURVES OF WEIGHT-LOSS, AND TEMPERATURE AT TOP OF TUBE. FIRE-TUBE TEST.

Various modifications of this test have been employed in Germany where some workers have stressed the need for a shorter sample. Schlegel found that 1 cm. by 1 cm. by 10 cm. samples gave more consistent results owing to their greater uniformity, and are more suitable for laboratory tests.

U.S. Bureau of Standards. Flame-Penetration Test **(C. R. Brown, Proc. Amer. Soc. Testing Materials, 1935, 35, Pt. II, 674).—Samples ¾ in. thick are supported horizontally on a ring stand 3 in. above the tip of a ⅜-in. Tirrill burner producing about 3,000 B.Th.U. per hour.** Observations are made of the temperature changes on the upper surface of the board and of the time for the flame to penetrate. Brown (J. Res. Nat. Bur. Stand. 1938, **20**, 217–239) showed that, as measured by the standard fire-endurance test, concentration of treatment had little effect on the fire-resistance of the partition, but that resistance depends on thickness and design; that time-results in the flame-penetration test vary directly with thickness, but the test has only a limited value as an indication of fire-endurance; and that fire-tube tests are definitely related with concentration of treatment.

Slow-Combustion Test.—J. F. Harkom and J. I. Dore (Proc. Amer. Wood Preservers' Assoc. 1933, 87) used this test to investigate the effect of low concentration of chemicals on glowing or slow combustion. Specimens of red pine 3½ in. long and 3½ in. diameter with a 1-in. hole bored in the centre, impregnated with chemicals and dried, were placed in a brass ring and suspended from a balance arm in such a way that the loss in weight up to 50% could be read directly on a chart. The centre of the specimen was heated for 6 minutes by a Bunsen burner directed up the hole. Flame-spread along the bottom and sides was prevented by a copper disc with a 1½-in. hole fitted on the base. Readings of loss in weight of the wood and the temperature of the brass ring were made every minute until combustion ceased or 50% of the wood was consumed. The most effectively treated substances merely charred during the heating period, untreated wood continued to flame, and wood treated with salts such as sodium dichromate continued to glow.

British Forest Products Research Laboratory Tests.—J. Bryan and L. S. Doman (Wood, 1940, **5**, 19) describe inflammability, flame-penetration and flame-spread tests which they have developed for measuring fire-resistance and have used for determining the comparative resistance of different species of timber. The *inflammability test*, based on Schlyter's test (Mitt. Fachaus. Holzfragen, 1938, No. 21, 84), uses two samples of wood 5 in. square held vertically ⅝ in. apart, one sample being 1½ in. higher than the other. A Bunsen flame ignites the face of the lower specimen and the time taken for this in turn to ignite the other specimen is recorded. Ignition is usually very distinct. In the *flame-penetration test* a sample 5 in. square and ½ in. thick is held horizontally 2 in. above the nozzle of a standardised blowpipe flame. The sample rotates in a horizontal plane in such a way that the centre of the flame describes a circle 1 in. diameter. This rotation was adopted because the results were much more consistent than those obtained with a fixed sample. The time required for the flame to penetrate the sample is noted. In the *rate of burning test* the sample consists of 50 half-inch cubes placed in a vertical iron tube 1½ in. diameter and 9 in. long, having an open grid at the lower end. The samples are ignited by a standardised gas flame which projects vertically down the tube, and is maintained for 60 seconds, or if, as in the case of some treated timber, ignition does not occur after 60 seconds, for 600 seconds. The tube is suspended on a balance arm, and the time for each 10% loss in weight is recorded, the time between a loss of 30% and 70% being used for comparison. The natural fire-resistance of over 70 species of timber was tested, and of these greenheart, gurjun, jarrah, laurel, padauk, pyinkado, teak, and white olivier show outstanding fire-resistant properties. Tests have also been carried out on specimens of wood treated with a number of fire-resisting solutions and coatings.

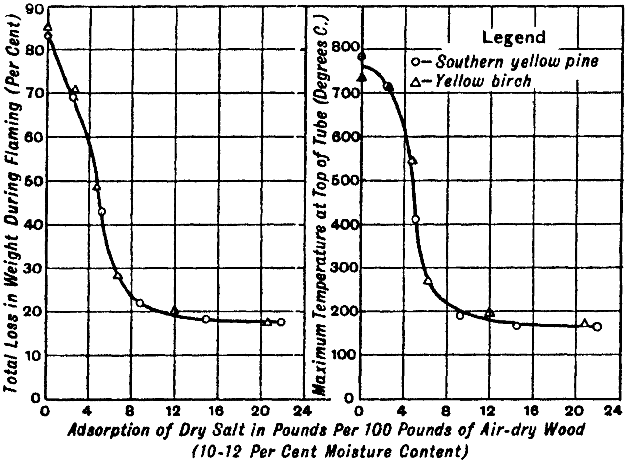


FIG. 3.—FIRE-RETARDING EFFECTIVENESS OF DIFFERENT ABSORPTIONS OF DI-AMMONIUM PHOSPHATE. FIRE-TUBE TEST.

Evaluation of Chemicals as Fire-Retardants.

The work of Gay-Lussac and Versmann and Oppenheim has already been mentioned. Prince (Proc. Amer. Wood Preservers' Assoc. 1914, 158) determined the temperature at which various treated timbers could be kept for 40 minutes without igniting. It was found impossible, under the conditions of test, to ignite wood treated with certain ammonium salts. Borax was effective, but other substances, including sodium carbonate and oxalic acid, besides being inefficient had a weakening effect on the wood. Banfield and Peck (Canad. Chem. Met. 1922, **6**, 172; Chem. and Ind. 1923, **42**, 155) measured ignition temperatures of wood in an electrically heated horizontal tube, and classified salts as fire-promoters or fire-retarders according as they lowered or raised the ignition temperature from the range 290–300°C. The fire-retarders were zinc, magnesium and calcium chlorides, ammonium sulphate and phosphate, borax, sodium silicate and zinc ammonium phosphate, ammonium phosphate being the best.

The most comprehensive series of tests made by a disinterested authority have been carried out by the U.S. Forest Products Laboratory using the fire-tube test (Proc. Amer. Wood Preservers' Assoc. 1930–1933, 1935). In all, about 130 chemicals or mixtures have been tested, mostly at 5% and 20% concentrations of anhydrous chemical in the air-dried wood, but 17 of the most promising were examined in sufficient detail for curves to be drawn relating concentration with loss of weight when flaming ceased and with maximum temperature at the top of the fire-tube. Typical curves, those for di-ammonium phosphate, are shown in Fig. 3, and a selection of the results is given in Table II.

The results of the tests on single chemicals show that mono- and di-ammonium phosphates,

Table II.—Results of U.S. Forest Products Laboratory Fire-Tube Tests on Wood.

Chemicals.	Adsorption of anhydrous chemical (air-dry wood).		Loss in weight when flaming ceased. %	Maximum temperature at top of fire-tube °C.	Tendency to glow. (Untreated = moderate.)
	lb./cu. ft.	lb /100 lb.			
None	—	—	83·5	782	Moderate
$(NH_4)_2HPO_4$	0·90	2·40	69·4	717	None
	1·84	5·37	43·4	412	,,
	3·23	6·00	21·8	191	,,
	5·15	14·64	17·9	168	,,
	7·25	22·04	17·1	165	,,
$(NH_4)H_2PO_4$	0·91	2·76	67·4	734	None
	1·84	6·30	56·9	607	,,
	2·60	7·48	26·5	254	,,
	4·99	13·92	19·0	196	,,
	7·29	19·89	15·7	184	,,
$(NH_4)_2SO_4$	1·35	4·41	70·4	732	Slight
	1·86	4·98	64·3	687	,,
	3·17	9·22	31·6	295	,,
	4·96	15·70	25·9	238	,,
	6·70	19·31	20·1	196	,,
NH_4Cl	5·36	15·74	24·2	231	Slight
$Na_2B_4O_7$	5·36	15·32	21·8	218	Moderate
H_3BO_3	5·42	15·10	66·8	714	None
	8·74	24·84	29·9	262	,,
$H_3BO_3:Na_2B_4O_7 = 60:40$	5·32	15·97	28·3	242	Slight
	7·14	21·14	19·1	203	None
$ZnCl_2$	5·08	14·85	20·7	173	Moderate
$Mg(H_2PO_4)_2$	5·45	14·94	54·5	579	None
	7·44	19·20	18·4	196	,,
$Mg(H_2PO_4)_2$ and NH_3(Gas)	3·85	10·76	21·6	204	None
	6·66	18·98	16·1	176	,,
$(NH_4)_2HPO_4:H_3BO_3 = 80:20$	5·38	14·93	16·2	205	None
$(NH_4)H_2PO_4:(NH_4)_2SO_4 = 36:64$	5·27	14·98	15·0	192	None
$(NH_4)H_2PO_4:(NH_4)_2SO_4 = 49:51$	5·54	15·38	14·8	195	None
$(NH_4)H_2PO_4:(NH_4)_2SO_4 = 63:37$	5·43	15·01	14·0	192	None
$(NH_4)_2CO_3$	5·34	14·64	77·5	743	Very slight
$NaC_2H_3O_2$	5·62	16·32	66·0	799	Slight
NH_4Br	4·44	11·61	18·5	185	None
$Al_2(SO_4)_3$	6·38	18·55	19·8	194	None
H_3PO_4	5·89	16·95	18·0	171	None
Na_3AsO_4	6·00	15·22	14·8	178	Moderate
Na_2HAsO_3	5·86	16·30	16·2	181	Slight

phosphoric acid, borax, sodium arsenate and arsenite, magnesium, lithium and ammonium chlorides and sodium molybdate gave the best results in reducing flaming, while ammonium sulphate, aluminium sulphate, ammonium bromide, and zinc chloride also had a marked effect. Of these, only three, the two ammonium phosphates and phosphoric acid, showed a high degree of effectiveness in reducing both flaming and glowing. Boric acid, also, was an effective glow retardant.

Di-ammonium phosphate gave the best results; mono-ammonium phosphate was almost as good; several mixtures of ammonium sulphate and mono-ammonium phosphate in widely different proportions and di-ammonium phosphate–boric acid and mono-ammonium phosphate–borax mixtures gave results very little inferior; a borax–boric acid mixture was also very effective.

Ammonium bromide, which has been used in Germany as a constituent of "*Cellon-Feuerschutz*" (A. Eichengrün, Z. angew. Chem. 1929, **42**, 214), does not appear to be as effective as the ammonium phosphates, and sodium acetate recommended by Schwalbe and Berling (Chem.-Ztg. 1932, **56**, 909) as a cheap fire retardant is shown to have little value.

Many of the treatments were designed to produce in the wood insoluble salts which would not be leached out on exposure to the weather, but no very effective fixing method has yet been devised. Treatments that at first seemed promising were found to owe this efficiency to soluble salts, such as ammonium phosphate, and a critical examination of most claims for complex mixtures will usually reveal that their value depends very largely on ammonium salts.

Glowing was studied by Harkom and Dore using the slow-combustion test and the best results obtained by them are given in Table III. The figures in the second and third columns represent, respectively, the highest concentration of anhydrous chemical, in lb. per cub. ft., which does not prevent combustion continuing to 50% loss in weight, and the lowest adsorption which does prevent it.

TABLE III.—SLOW-COMBUSTION TEST RESULTS.

Chemical.	Effectiveness.		Mean, lb./-cu. ft.	Exceptions, lb./cu. ft.
	Min., lb./-cu. ft.	Max., lb./-cu. ft.		
H_3PO_4	—	0·17	0·17	
$(NH_4)_2HPO_4$	—	0·17	0·17	
$(NH_4)HB_4O_7$	0·16	0·32	0·24	0·15 effective.
$(NH_4)_2SO_4$	0·33	0·38	0·35	0·16 effective.
NH_4Cl	—	0·37	0·37	
$(NH_4)H_2PO_4$	0·34	0·49	0·41	0·34 effective. 0·17 (37% wt. loss).
$(NH_4)_3PO_4$	0·34	0·57	0·45	0·17 effective.
KNO_2	—	0·48	0·48	
$MgCl_2$	—	0·52	0·52	
$ZnCl_2$	—	0·62	0·62	

These figures indicate the great efficiency of certain substances in preventing glowing. These reduced combustions do not, however, appreciably increase the resistance to flaming.

The property of glow-prevention is utilised by many manufacturers of matches, and ordinary impregnated matches contain small amounts of salts such as mono-ammonium phosphate which not only prevent the charcoal glowing, but give it sufficient rigidity to prevent the hot head of the match falling off during burning. The wood burns but flaming is increased by dipping the match in wax.

Methods of Fireproofing Timber.

All the chemicals generally used for fireproofing wood are soluble in water, and they are injected into the wood as an aqueous solution. The methods employed are essentially similar to those which have been developed by the wood-preserving industry, for treating wood with creosote, or particularly with preservative salts.

Wood that has to pass stringent acceptance tests must be completely impregnated with the retardant, and except in cases where thin sections are being treated the only satisfactory method is that employing impregnation under pressure. Even when complete impregnation is not demanded this is the only method by which adequate protection of thick or impregnation-resisting timbers can be achieved.

Considerable protection is afforded even when the interior is not impregnated and it is still an open question whether any advantage is gained by insisting on the complete impregnation of thick baulks or beams, which are not liable to subsequent splintering, as the interior would be well insulated by the layer of hard charcoal produced on the surface of fireproofed timber.

If, however, timber is to be cut or machined, complete impregnation is generally essential, but as far as practicable, all cutting should be done before impregnation. Where the wood has to be painted or varnished some planing or sanding is necessary after treatment, but this should be as light as possible, as the outer layers contain the highest quantity of salt. Considerable protection may be given to lighter sections, or to the more easily impregnated woods by steeping treatments, and even surface treatments, such as brushing and spraying, may serve to prevent the start of a fire, or its spread in the initial stages.

IMPREGNATION UNDER PRESSURE.—The full-cell process is employed after preliminary steam and vacuum treatment. Results of the fire-tube test have shown that when the most effective fire-retardants are employed maximum protection is obtained when wood contains 12% or more of its weight of the chemical, and experience has shown that to achieve this a 15% solution may generally be used.

The plant employed is similar to that used for creosoted timber; it consists of the following units: (1) A mixing and storage tank heated, for example, by steam coils and fitted with a stirrer; the capacity of this tank must be greater than that of the pressure cylinders and it is desirable that it should be at a higher level than the rest of the plant. (2) One or more pressure impregnation cylinders of steel or cast iron designed for a working pressure of at least 150, and preferably 200, lb. per sq. in. (gauge). Safety release valves and pressure and vacuum gauges should be fitted. (3) A hydraulic reciprocating pump capable of maintaining a pressure of 150–200 lb. per sq. in., and of emptying the cylinders in a relatively short time, or a compressed air supply. (4) A vacuum pump capable of exhausting the cylinders to a vacuum of 25–29 in. of mercury in about 1 hr. (5) A supply of steam at 20–25 lb. per sq. in. (gauge) pressure.

Owing to the wide variability in the resistance of timbers to impregnation no rigid schedule of treatment can be laid down, and details of the various steps described should be modified as a result of experience to suit the type of timber and the purpose for which it is required.

The process consists of the following stages :

Loading the Cylinders. — The timbers, separated by slats, are stacked on a trolley; this is run into the cylinder, which is then closed. Before stacking, several pieces of timber, representative of the batch, should be weighed and marked; they are weighed again after treatment and from the increase in weight the percentage adsorption of chemical can be calculated. The average will indicate whether the treatment has been sufficient. The total amount of solution adsorbed by the batch may be measured by observing the level of the storage tank before and after applying pressure. In addition, thoroughly impregnated timber takes up nearly its own weight of solution and the increase in density is sufficiently striking for the experienced operator to be able to tell whether treatment has been satisfactory, and to pick out planks which are insufficiently treated. These can then be separated from the remainder of the batch and re-treated.

Preparation of the Solution.—Common timbers will adsorb, on an average, about 80% of their air-dry weight of solution. In such cases it is necessary to use a 15% solution if the concentration of salts in the wood is to be about 12%. For more resistant timbers, and where complete impregnation is not required, stronger solutions, *e.g.* up to 20%, may be used. The control of the concentration of the solution is most easily effected by measuring the density. Table V shows the density of mono-ammonium phosphate solutions for the temperature and concentration range normally used in fireproofing.

TABLE V.—DENSITY OF MONO-AMMONIUM PHOSPHATE SOLUTIONS.

Temp.		Concentration (by weight).							
		10%		15%		20%		30%	
°F.	°C.	sp. gr.	°Tw.	sp. gr.	°Tw.	sp. gr.	°Tw.	sp. gr.	°Tw.
68	20	1·058	11·6	1·086	17·2	1·115	23·0	1·181	36·2
86	30	1·054	10·8	1·083	16·6	1·113	22·6	1·178	35·6
122	50	1·050	10·0	1·077	15·4	1·108	21·6	1·167	33·4
158	70	1·042	8·5	1·070	14·0	1·100	20·0	1·159	31·8
194	90	1·034	6·8	1·063	12·6	1·092	18·4	1·150	30·0

The temperature of solution may suitably be about 70°C.

Steaming.—Live steam at 20–25 lb. pressure is blown into the cylinder, the air release valve and drain valve remaining open until steam begins to blow out. These valves are then closed, and condensed steam-water is blown out at intervals. Pressure should preferably be allowed to build up slowly, reaching its maximum after about 1 hour and being maintained at the maximum for 1 hour or more, according to the type of wood being treated.

One effect of steaming is to raise the temperature of the wood, but it may also modify the wood structure. In practice the effect is that much more even adsorption of a batch is achieved. Steam temperature rapidly increases with pressure, and high temperature is injurious to wood; certain species are particularly sensitive to it. Steaming should, therefore, be as mild as possible, consistent with good adsorption and penetration.

Vacuum.—Immediately after steaming vacuum is applied. This serves to remove condensed moisture and air from the outer layers of the wood, so facilitating the entrance of the preservative and increasing the effective pressure. The duration of the vacuum should not be prolonged beyond one hour as otherwise the beneficial effect of wood temperature on penetration will be lost.

Pressure.—When admitting air, the cylinder is completely filled with the hot solution of fire-retardant and then additional solution is forced in until the desired pressure is attained. Generally a pressure of 100–150 lb. per sq. in. is sufficient, but with very resistant timbers pressures of 200 lb. per sq. in., or even higher, may be applied.

The duration of the pressure treatment depends on the pressure, the species of wood, whether heartwood or sapwood is being treated, and timber sizes. Prolonged impregnation at a low pressure is preferable to rapid impregnation at a high pressure. Most timbers can be impregnated by applying a pressure of 150 lb. per sq. in. and the time required may be from 2 to 24 hours. When very resistant timbers are being treated the period of impregnation may have to be considerably extended, and pressures of 200 or even 300 lb. per sq. in. may be necessary to secure thorough impregnation. Great care must be taken in such cases to guard against "collapse" of the timber, particularly after steaming, and pressures of more than 200 lb. per sq. in. should only be used after careful experiment.

The American Wood Preservers' Assoc. "Manual of Recommended Practice" includes standard specifications for the preservative treatment of ties, timber and lumber, excluding Douglas fir, larch and tamarack (34b and 35c), and of Douglas fir ties (38a), by pressure processes. The treatment of timber with salt ($ZnCl_2$) specified in 34b and 35c is: "Air-seasoned timber may be steamed in the cylinder for not less than one hour, nor more than two hours, at a pressure of not more than 20 lb. per sq. in. After steaming is completed a vacuum of at least 22 in. shall be maintained for not less than 15 minutes or until the wood is as dry and free of air as practicable. If the vacuum is broken while the condensate is being drained from the cylinder a second vacuum as high as the first shall be created. The preservative shall be introduced without breaking the vacuum until the cylinder is filled. The pressure shall then be raised to and maintained at a minimum of 100 lb. per sq. in. until the quantity of preservative to insure the final retention stipulated is injected into the timber, or until less than 5% of the total quantity required has been injected during the latter half of one hour throughout which the rate of injection has persistently decreased while the pressure has been held continuously at 125 lb. or more per sq. in. The temperature of the preservative during the pressure period shall be not less than 140°F. nor more than 200°F. and shall average at least 150°F."

For Douglas fir ties the conditions are somewhat modified. Steaming is used for heating purposes only: it may be continued for 1 to 2 hours at a temperature of not more than 250°F. The preservative is introduced at 160–200°F. and the pressure is maintained at between 125 and 175 lb. per sq. in. until the required amount of preservative solution has been injected.

Drying.—Fireproofed timber cannot be dried in the open without protection because of the danger of leaching the salts out of the wood. It may be partly dried by stacking in sheds. Much of the wood which is fireproofed is required for interior use, and its moisture content has to be reduced to 6–7% to avoid difficulties due to shrinkage after installation. This can only be achieved by kiln-drying, and some type of drying kiln is an essential part of a fireproofing plant. Details are described elsewhere (Forest Products Research Lab. D.S.I.R. Special Reports Nos. 2 and 3).

The basic principle of kiln-drying is the rapid circulation of hot, moist air through the stacks of timber: the high temperature induces high moisture transfer from the centre to the surface, and the high humidity prevents rapid drying of the surface which would lead to checking. It is therefore necessary to control the temperature and humidity of the kiln within narrow limits, and to vary these as drying proceeds in accordance with a fixed schedule. Each class of timber requires special treatment and schedules for all the common timbers have been worked out at the Forest Products Research Laboratories.

In drying fireproofed timber certain specific factors need special consideration. The timber is excessively wet, and careful stacking is essential if warping is to be avoided. All effective fire-retardants accelerate carbonisation of the wood, and unless care is taken to avoid high kiln-temperatures the wood is darkened.

Experience has shown that fireproofed wood can be dried without checking more rapidly than natural wood, that is, the humidity of the kiln may be appreciably lower than usual. In this connection, work carried out at the U.S. Forest Products Laboratory is of interest. According to S. H. Kahn (Wood, 1940, **5**, 44) seasoning can be greatly accelerated by soaking timber in concentrated solutions of salts, such as sodium chloride or mono-ammonium phosphate, so that the outer layers are impregnated. Losses, by checking, of timbers which are normally very difficult to dry are very much reduced. Kahn suggests that the effect is due to the fact that water evaporates more rapidly in a pure state than from a saturated salt solution, and that therefore the surface layers retain their water content, while the centre is drying; drying is from the inside out, instead of from the outside in.

This mechanism may in part account for the greater ease with which fireproofed wood is dried, but it seems more likely that, as a result of the pressure treatment, wood which has been fireproofed with an aqueous solution will have a more open structure and capillary effects in the drying process will predominate.

It seems advisable, therefore, to modify the schedules for drying fireproofed timber, so that the drying temperature is 5–10°C. below the temperature used for untreated wood and the humidity is reduced appreciably below that of the normal schedule.

HOT-AND-COLD SOAKING.—Adsorption of cold solutions by softwoods is a slow process. Adsorption of hot solutions is much more rapid, but the best effect is obtained by a hot-and-cold process. In this the timber is immersed in a hot solution (90–100°C.) and then either allowed to cool while immersed in the solution, or rapidly transferred to a cold solution. The time required depends on the type and thickness of the timber, but effective protection can be given to yellow deal, for example, by immersion for 8 hours in a hot 20% solution of ammonium phosphate followed by cooling for 8 hours. Complete impregnation may not always be effected, but the outer layer would be fireproof. Preliminary tests on mine timbers described in the Report on Research Work carried out in the Department of Mining of Sheffield University, 1931–1932, showed that, under the conditions of the test, soaking wood in 1:5 solution of ammonium phosphate in water for three days with subsequent drying renders timber practically fireproof and the mere painting or spraying of timber with this solution has a preventative effect.

Owing to the fact that impregnation may not be complete, the timber should be shaped and cut to its final size before immersion.

PAINTING OR SPRAY-COATING.—Solutions of fireproofing salts, such as ammonium phosphate, may be applied to adsorbent unpainted surfaces. Solutions may, preferably, be hot and should be concentrated, *e.g.* 30%. It is advantageous to apply three coats, the second after the first is almost dry ; preferably 4 lb. of fire-retardant should be applied per 100 sq. ft. of surface. In order to ensure maximum penetration a wetting agent may be incorporated in the solution, and adhesion of the crystal film is greatly assisted by including a colloid, such as gum arabic, in the solution, the amount used being about 10% of the weight of the salt.

It must be emphasised that surface treatments do not give a high degree of protection in an intense fire, but they do give effective protection in the initial stages and, moreover, modify the surface layers in the same way as impregnation does, so that the formation of inflammable gases is reduced and a hard, firm charcoal is formed.

Secondary Effects of Fire-Retardants on Timber.

Hygroscopicity.—If wood becomes hygroscopic as a result of treatment difficulties will arise, particularly on account of corrosion and peeling of paint.

The relative humidity of closed systems containing saturated solutions of certain salts is given in Table IV. In atmospheres of higher humidities than these the salts adsorb moisture.

As the monthly average relative humidity in this country (Kew) from October to March varies from 81–88 it is inadvisable to use mixtures of salts which become moist at humidities lower than this. Here mono-ammonium phosphate is particularly valuable. In conditioned atmospheres, however, or heated interiors, ammonium chloride or mixtures of

TABLE IV.—RELATIVE HUMIDITY AT WHICH SALTS ADSORB MOISTURE.

Solid phase.	R.H. 20°C., %	Solid phase.	R.H. 20°C., %	Solid phase.	R.H. 30°C., %
$H_3PO_4 \cdot \frac{1}{2}H_2O$.	9	$(NH_4)_2SO_4$	81·0	$(NH_4)H_2PO_4 + (NH_4)_2SO_4$	75·8
$ZnCl_2 \cdot 1\frac{1}{2}H_2O$.	10	$(NH_4)H_2PO_4$	93·1	$NH_4Cl + (NH_4)H_2PO_4$	74·4
NH_4Cl . . .	79·5			$NH_4Cl + (NH_4)_2SO_4$	71·5

ammonium phosphate and sulphate may be safely used, particularly if the surfaces are afterwards painted. As already stated the Bachert process, which has been extensively used in America, utilises an ammonium sulphate–phosphate mixture.

Corrosion.—Hygroscopicity is one of the main factors. S. G. Wedenkin (Russo-German Soc. for Culture and Technology, Trans. Gen. Conf. Standardisation and Manuf. New Build. Mats., Moscow, 1932, 17) found $ZnCl_2$ unsuitable for fireproofing locomotive depots because of corrosion. Ammonium chloride gave better results but led to rapid rusting; ammonium sulphate was found suitable when sodium phosphate was present as corrosion inhibitor. R. H. Baechler (Proc. Amer. Wood Preservers' Assoc. 1939, **35**, 56) describes tests on the corrosion of fittings in contact with wood impregnated with zinc chloride. The amount of salt present (1·5 lb. per cu. ft.) was small compared with that which would be needed for fireproofing (5 lb. per cu. ft.). He found that corrosion of common wire nails in wood treated with zinc chloride and exposed to a moderately humid interior, or to outside conditions, is not appreciably greater than that occurring in untreated wood provided the treated wood is seasoned before the nails are driven in.

Schlegel reports tests in which tinplate strips were nailed on to the wood impregnated with solutions of various salts (1 mol./l.) and stored in an open shed for 6 months. Ammonium phosphate, ammonium sulphate, lithium chloride, magnesium chloride and sodium sulphate did not cause any change in weight. Ammonium chloride, bromide, and iodide caused increases of 2, 3 and 4% respectively. Other salts caused losses, zinc chloride 0·1%, aluminium sulphate 0·1%, and sodium acetate 0·75%.

A series of corrosion tests comparing the effects of pure and commercial mono-ammonium phosphate and mono-ammonium phosphate–sulphate mixtures is described in "*Faspos*—The Fireproofing of Wood" (Imperial Chemical Industries). Immersion tests on cold 20% solutions showed only slight differences between all these substances, average loss in thickness per year for mild steel being 0·32 and 0·25 mm. for commercial and pure salts respectively during the first 8 weeks, and 0·15 mm. for both at the end of the year. Corrosion of copper and brass was very small, averaging 0·01 and 0·02 mm. thickness per year respectively. Timber impregnated with mono-ammonium phosphate and kept in an atmosphere of controlled humidity (85% at 28°C.) for 8 weeks remained quite dry, and mild steel plates bolted thereto were not corroded. Where the phosphate–sulphate mixture was used, however, the timber became very damp, there was marked corrosion of the metal, and evidence of mould growth on the surface of the wood. Similar test-pieces were exposed to the weather and, after 3 weeks, corrosion had commenced on those treated with the mixture; after 1 year it was very advanced. On wood treated with mono-ammonium phosphate there was no corrosion of the plates in 3 weeks, and after 1 year it was less than that on a plate attached to untreated wood. When stored in a laboratory cupboard all the samples remained dry and the slight corrosion which occurred was the same in all cases, including the sample in which the wood was untreated. Addition of boric acid to the solutions had no noticeable effect on corrosion.

Hunt and Garratt mention that corrosion of plant may occur with ammonium phosphate, but the above immersion test would indicate that it is likely to be small, and that after the first few weeks a protective film is formed.

Glueing.—Truax, Harrison and Baechler (Proc. Amer. Wood Preservers' Assoc. 1935, 231) reported glueing tests. They showed that the ammonium phosphates offered little or no interference with animal glue, somewhat more with vegetable glue, and rather seriously interfered with glueing with low-alkaline casein glues. Sponging the surfaces of di-ammonium phosphate-treated wood with 10% caustic soda solution before glueing improved joint strength, particularly with the low-alkaline casein glue. The chlorides of ammonia, zinc and magnesium also interfered with the making of joints with casein glues, and borax with vegetable glue.

Painting and Varnishing.—Experience has shown that fireproofed wood can, in general, be painted, varnished, and French polished in exactly the same way as ordinary wood. It has been noted, however, that some finishes require a primer. Silicate paints cannot, for example, be used direct on wood treated with salts such as ammonium phosphate, owing to chemical reaction.

Machining.—The presence of fire-retardant salts in the wood renders it more difficult to plane and saw than untreated material, since the crystals cause the cutting edges to wear more rapidly. The use of tools specially designed for the purpose, however, may minimise the trouble.

Preservative Action.—There is obviously an advantage in using a solution which both preserves and fireproofs the wood. Zinc chloride in low concentrations (about ½ lb./cu. ft.) is widely used as a preservative, but in the higher concentration (5 lb./cu. ft.) necessary for fireproofing it has a weakening effect on wood. Various salts are toxic to dry-rot fungi, and numerous mixtures have been proposed from time to time. Some of the most effective are the silicofluorides. Commercial mono-ammonium phosphate produced from rock phosphate contains appreciable quantities of sodium silicofluoride, and wood fireproofed with this has been shown to be resistant to dry rot. The "*Oxylene*" mixture contains boric acid, which serves the same purpose.

Stability.—The majority of salts commonly used for fireproofing are stable, and the treatment, particularly when finished with paint or varnish, is permanent. This was demonstrated in 1931 to officials of the New York and Philadelphia building departments by a standard door test on a 1¾-in. flush door made from 26-year-old fireproofed hotel doors (Proc. Amer. Wood Preservers' Assoc. 1935, 221).

Fireproofing of Other Materials.

Plywood.—Three-ply and five-ply wood are fairly easy to impregnate. Pressure impregnation is probably the most satisfactory. Treatment for ¼ hour with a cold 15–20% solution of fire-retardant without any steaming or vacuum has proved sufficient for fireproofing.

The hot-and-cold steeping process may be employed, but the operation of the process requires much greater care than is required with ordinary timber, as the hot solution may have a detrimental effect on the glue. Many of the better quality plywoods have waterproof cements or a resin film, which will withstand the action of the hot solution. Great care must be taken in stacking plywood for drying; wet plywood is very flexible and unless it is dried flat, will usually warp badly. It is also advisable to dry the material at temperatures as low as possible.

Reeds.—The surface of reeds is very impervious but, by using a solution containing a colloid such as gum arabic, a film of fire-retardant will be produced on the reed. The process, then, consists in immersing the reeds in a 20% solution, preferably hot, of fire-retardant containing 20% by weight of the colloid, allowing to drain and dry. In use as a thatch, the salts are washed from the outer surface, but the lower layers retain their fire-resistance. As thatch is usually 12–15 in. thick, the loss of fireproofing effect by weathering is small.

Fireproof Paints.

Although impregnation with fire-retardant salts is the most effective method of increasing the fire-resistance of timber, considerable protection may be given by coating it with an inert material which serves as an insulation from the fire, and so prevents ingress of oxygen.

Among the simplest and cheapest coatings are limewash and distemper, and these give definite, though transitory, protection.

The value of calcium sulphate plasters as heat-insulating coatings for wood is well known, and of these the dense anhydrite plaster is particularly effective. A product recently developed containing anhydrite plaster and a small percentage of organic adhesive, is suitable for application by brush or spray, and coatings one-sixteenth of an inch thick have been shown to be sufficient to prevent ignition of wood by an incendiary bomb.

Water glass or sodium and potassium silicates appears to be the most popular coating, but to be effective this must contain a filler such as asbestos, clay, metallic oxides (also as pigments), or chalk. E. Kunze (Farbe u. Lack, 1934, 134, 147) compared the fire-resistance of three types of silicate paint. Silicate solution alone gave little protection, better results were obtained when powdered asbestos was included as a filler, but the best results were obtained using a mixture of silicate, asbestos, casein, caustic soda and borax. Greiner (Seifens.-Ztg. 1938, **65**, 519) gives numerous formulæ for silicate paints.

Sodium silicate, when first applied, has the property of blistering under the action of heat and so forming an effective insulating layer. Unfortunately this property is lost on ageing. More recently organic foam-forming materials have been used. Thus "*Locron*" is stated to form a very voluminous foam when heated. B.P. 334408 granted to I.G. Farbenind. refers to the use of a solution or suspension of fire-retardants and urea–formaldehyde condensation products which adhere to the material and prevent crystallisation.

Chlorinated rubber paints have recently come to the fore as non-inflammable paints and they are suitable for interior decoration.

Prince (H. F. Weiss, "The Preservation of Structural Timbers," 1916, p. 336) investigated the relative inflammability of unpainted and painted shingles and sidings and found that a paint made of zinc borate (7 lb.), chrome green pigment (2½ lb.) and boiled linseed oil (1 gallon) had good fire-resistant properties.

By means of a modified fire-tube apparatus Metz determined the fire-resistance of wood coated with paints of four different types. Protection given to thin slats increased in the order: chlorinated rubber paint, pigmented sodium silicate, ammonium salts, and an organic foam-forming material, the last named giving considerable protection. No noticeable increase in the fire-resistance of thick beams was found when they were painted.

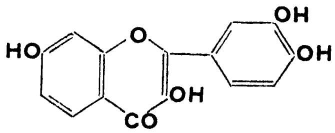
In connection with the preparation of fire-resistant varnishes Butcher (Chem. Trade J. 1931, **88**, 248) states that di-ammonium phosphate to the extent of 5% may be added without making the film opaque. Sodium tungstate ground in linseed oil is also said to have good fire-retardant properties.

Literature.—An extensive bibliography is given in Proc. Amer. Wood Preservers' Assoc. 1936, 429–475. For the last few years this publication has contained a review of prominent articles on fireproofing published during the year. A summary of nearly 500 references, mainly to patents, is included in the Second Report of the Fabrics Co-ordinating Research Committee, D.S.I.R. 1930, Appendix I. References to fireproof paints are given in Science Library Bibliographical Series No. 171, Science Museum, South Kensington, 1935.

I. C. R.

FISCHER'S SALT (*v.* Vol. III, 219*b*).

FISETIN,



is a flavone pigment present in Young Fustic. It has been synthesised from veratric aldehyde and ω-methoxyresacetophenone (Allan and Robinson, J.C.S. 1926, 2334; *cf.* Kostanecki, Lampe and Tambor, Ber. 1904, **37**, 784).

FISH MEAL (*v.* Vol. IV, 597*b*).

FISH OILS.—This term usually includes fatty oils derived not only from fish but also from marine mammals, such as whales and seals. Such grouping is logical enough since not only is the habitat the same but the fats, with few exceptions, have fairly similar characteristics and compositions. Moreover, they form a group which is strikingly different from the other common commercial fats, such as the tallows, vegetable fats, etc.

The fish oils of commerce may be classified broadly into three categories: (*a*) fish-liver oils, such as cod- and halibut-liver oils; (*b*) fish-body oils, such as menhaden and sardine oils; and (*c*) marine mammal oils, such as whale and seal oils. Fish-liver oils have already been discussed (*v.* COD-LIVER OIL), and will be dealt with only briefly here. With the exception of a few specially valuable medicinal oils of high vitamin potency, they are all prepared by rendering the whole livers with live steam, as described. The exceptions are oils from the livers of such fish as halibut, swordfish, tuna, etc., which cannot be rendered by steaming and are usually obtained by processes involving complete peptisation of the liver protein. The chief liver oil of commerce is pre-eminently cod-liver oil, but appreciable quantities of shark and other fish-liver oils are also prepared.

The fish-body oils may be derived from individual species, in which case they are marketed under the appropriate names, or from mixed species, when they are usually sold simply as fish oil. The commonest individual oils are menhaden, sardine, pilchard, herring and salmon (from offal, rather than flesh). The processes of reduction are very similar and consist in cooking the fish with live steam, pressing the cooked mass and separating the oil from the expressed emulsion. The manufacture of these oils will be separately described.

The chief marine mammal oils of commerce are the whale oils, particularly those from the blue and fin whales, with lesser quantities of sperm whale oil.

Menhaden Oil.—The menhaden (*Brevoortia tyrannus*) is related to, and closely resembles the herring. It is caught seasonally along the Atlantic coast of the U.S.A., solely for conversion into oil and meal, and does not appear ever to have been caught for food. The fish migrate in large shoals and the fishing season depends chiefly on water temperature, lasting longer in the south than in the north. Menhaden oil has been manufactured since about 1812. In the earliest processes it was obtained by allowing the fish to rot in barrels, the oil being skimmed from the surface; the yield and quality were, as would be expected, very poor. Later the fish were boiled in open vessels over fires, the oil again being skimmed from the surface. Larger vessels heated with live steam replaced these and the residues (" chum ") were also pressed, giving a better yield of oil.

The modern industry is controlled by legislation in the different states. The fishing is done from specially-built ships which locate shoals of menhaden, enclose them in purse-seine nets and ladle the fish aboard. As the fish deteriorate rapidly, the vessels usually return to port every 24 hours. The factories are situated at the waterside and the fish are unloaded directly from the hold into the factory by means of bucket elevators, either going straight to the cookers or to temporary storage.

The cooker consists of a stationary cylinder about 2½ ft. in diameter and between 25 and 40 ft. long. The fish enter at one end through a hopper and are propelled along it to the outlet by means of blades attached to a revolving central shaft. Live steam is admitted either through jets in the cylinder wall or perforations in the central shaft. The time of cooking depends on the condition of the fish, being less for soft or small material, but is of the order of 15 minutes. The plant runs continuously and the cooked mass, including condensed steam, is conveyed directly to continuous-screw presses. These consist of a worm, tapered so that the contents are subjected to a steadily increasing pressure as they pass along, turning inside a cylindrical casing composed of horizontal slats with narrow spaces between. The pressed-out liquid—an emulsion of oil, aqueous liquors and much suspended solid—collects on the press-room floor and drains away to the first of a series of open settling tanks. Here most of the coarser suspended matter settles out and a gradual separation of oil and aqueous liquor is effected. The oil, still containing emulsified water and solids, is passed to a " cooking tank " where it is heated by means of open or closed steam coils until the emulsion breaks and the freed oil can be skimmed off. The small amount of emulsified oil remaining, known as " gurry," is treated in various ways, including rotting to decompose protein matter and so break the emulsion. This gives a low-grade oil. Gurry is sometimes filter-pressed. The meal from the screw presses is either dried or acidulated with sulphuric acid. It was formerly used only as a fertiliser, but recently the dried product has come into increasing use as a feeding stuff. A full account of the menhaden industry has been written by Harrison (U.S. Bur. Fish. Investig. Rept., No. 1, 1931), in which the steps of the process are critically examined and suggestions made for improving them (*see also* Harrison and Pottinger, *ibid.* No. 4, 1931).

Sardine Oil is prepared from different species of sardine and related fish in various parts of the world, usually in connection with the canning of sardines. The bulk of the sardine oil of commerce, however, comes from California and Japan. The Japanese product is made largely from a pilchard (*Clupanodon melanostocta*), but often mixed related species are employed, in which case the oil is usually sold as Japanese fish oil. It will be sufficient to describe the manufacture of the Californian product which is obtained from a true sardine, *Sardinia cærulea.* The first oils were made from offal from canning factories and were produced as a side-line in factories dealing with slaughterhouse offal. The first Californian plant for the sole treatment of fish commenced in 1914 and used a process including cooking and drying the fish in one operation, followed by gasoline extraction of the oil. The method did not find general favour and has not been used since 1920. Apart from this solvent process, the method from the beginning has been cooking with live steam, followed by pressing, the press liquors until 1927 being invariably dealt with by flotation through a series of settling tanks, as with menhaden oil. The first centrifugal system for dealing with press liquors was installed in 1927, and since then this method has found increasing use. Other more recent items include the "foots machine" and the vibrating screen (*vide infra*).

Prior to 1930, the only material available in quantity for oil and meal production was offal from the canneries, but it should be remembered that such offal included all soft and damaged whole fish, as well as those of a size unsuitable for canning, and, in fact, the amount of offal was usually about 40–50% of the total catch (Scofield, California Fish and Game, 1938, **24**, 210). The profits from the oil and meal industry led to special permits being issued in 1930 for the reduction of a certain additional percentage of whole fish and about 1932 the introduction of factory ships operating outside territorial waters and catching sardines purely for reduction to oil and meal, caused the breakdown of the legislative attempts to restrict the industry to one of by-products. The result has been drastic overfishing with the exhaustion of supply already in sight (Scofield, *l.c.*; Clark, *ibid.* 1939, **25**, 172).

The modern cookers are essentially the same as the menhaden cookers, the fish being cooked for about 20–25 minutes at steam pressures ranging from 3–25 lb. Some 3 ft. from the discharge end of the cooker, the bottom half of the shell is replaced by a screen to carry away any freed oil and moisture. The cooked mass falls directly into a continuous screw press, situated below the cooker, and is dealt with while still hot. Sardine presses are similar to those used in the menhaden industry, but the shell is a tube perforated with holes instead of being constructed of slats. The solid from the press is dried, ground and sold as a feeding stuff.

The press liquors are dealt with in various ways. The majority of plant still use the settling-tank system, involving normally about five tanks in series, two or more being provided with steam pipes to maintain a temperature of 165°F. A final cooking of the oil to break the emulsion, as is done with menhaden oil, is not necessary with sardine oil. Some plant incorporate vibrating screens to remove much of the suspended solid, and centrifuges to assist in the last stages. The "foots machine" is a combined screening and pressing device for dealing with the sludge from the settling tanks.

The all-centrifugal process involves two steps. The first is the removal of the bulk of the solids in a solid basket centrifuge, usually called the bulk centrifuge. In a typical apparatus the basket may be about 18 in. deep, and of 40 in. diameter, dealing with about 3000 gallons of press liquor per hour. The cleared liquid, removed from the centre of the basket by a skimming pipe is heated to 200°F. by live steam and fed into high-speed centrifugal oil and water separators. Here the remaining solids are also removed and the modern machines have an automatic sludge-unloading arrangement which operates at full running speed. Some manufacturers replace the bulk centrifuge by a vibrating screen or other device and merely use the high-speed centrifuge. For further details of the Californian sardine oil industry, *see* Hatton and Smalley (California Fish and Game, 1938, **24**, 391).

Pilchard Oil is made in various parts of the world from different species of pilchards, particularly in British Columbia from *Sardinops cærulea.* This Canadian industry is a modern one, the commercial canning of pilchards having been begun in 1917. From the first the quantities of fish landed have been in excess of the canning requirements and in 1925 reduction machinery was installed. To-day 95% of the pilchards caught in British Columbia are reduced to oil and meal. The fishing is seasonal, from July to September, with occasional catches in June and October, and is conducted similarly to the menhaden fishing.

At the factories the fish are unloaded directly by means of bucket or slat elevators into storage bins, from which they pass to continuous cookers of the type already described. The cooked material is pressed in a continuous screw press of the type used in the sardine industry and the liquors are dealt with either by a series of settling tanks, or, in the most up-to-date plant, by centrifugal apparatus. In the settling tank method, the final aqueous liquors which are run to waste contain from 0·5 to 1% oil and the total loss is considerable, just as it is in the menhaden and sardine oil industries. One type of centrifuge in use is a high-speed machine of high sludge-capacity, from which the solid can be dumped whilst the machine is in operation. No preliminary bulk centrifuge is required, the press liquors merely being warmed to about 175°F. and passed directly through the centrifuge at a rate of about 400 gallons per hour. The oil so obtained is ready for immediate storage. Further details of the industry are given by Hart (Biol. Board Canada Bull. No. **36**, 1933), whilst Brocklesby and Bailey (*ibid.* No. **46**, 1935) discuss methods of improving the quality of the product obtained. The losses of oil in effluent waters are considered by Beall (*ibid.* No. **35**, 1933) and Hart, Marshall and Beall (*ibid.* No. **39**, 1933).

Herring Oil is produced in relatively small quantities from offal at canning factories, etc., and in larger amounts from whole fish in certain countries, such as Norway, Sweden, Iceland and Alaska. In Norway, for instance, the larger part of the annual catch of herring is converted into meal and oil, there being over sixty factories for this purpose. It is mainly the large winter catch which is thus used and between 300,000 and 400,000 tons are reduced annually. The oil tends to be of poorer quality than such oils as menhaden, sardine and pilchard, as the herring are often obtained in such large quantities that much material has to be stored for long periods (up to several months), preserved with salt and chloride of lime, before the plant can deal with it. This method has the advantage, however, of keeping the plant running over a large part of the year. As a result of this storage, the oil varies in colour from pale yellow to dark brown. The processes are very similar to those already described, including cooking with live steam in continuous cookers, pressing in a continuous screw press dealing with the press liquors either by straining and centrifuging or by means of settling tanks. The cooker is usually of a design rather different from that already described, consisting of a long shallow trough rather than a cylinder. The time of cooking varies with the freshness of the material and if the fish are incorrectly cooked the press liquors form an unbreakable emulsion. Ludorff (Fette u. Seifen, 1937, **44**, 416), describing the industry in Iceland, states that it is necessary to store all the herring used (with salt) for some 10–14 days before cooking if intractable emulsions are to be avoided. This salting is done in large " bins " and during the storage period a considerable amount of oil is freed and is collected through special channels in the bottom of the bins.

Salmon Oil is made entirely from offal from the canning and curing industries, principally on the Pacific coasts of the U.S.A. and Canada. Only a very small fraction of the total waste is so utilised, due mainly to the isolated positions of many of the canneries, the shortness of the seasons (especially in Alaska and the far north) and the difficulty of transport to a central reduction plant. The offal consists of heads, tails and fins, viscera including livers and gonads, and in the case of larger fish, a portion of the body and the nape bones. It usually amounts to about 33–35% of the total weight. The principal species used are the Alaska red salmon (sockeye), *Oncorhynchus nerka*; the Pink (humpback) salmon, *O. gorbuscha*; the Coho (silver) salmon, *O. kisutch* and the Chum (Keta) salmon, *O. keta.* The oil produced at the different factories varies in appearance and properties according to the preponderating species being canned at that factory. The processes are substantially as already described, involving cooking with live steam (usually in batch cookers, rather than continuous apparatus), pressing or centrifuging the cooked mass and separation of the liquors either by settling tanks or by centrifugal means. The residue is usually converted into meal, as with menhaden, sardine, pilchard and herring. Further details can be obtained from Tressler (" Marine Products of Commerce," 1923, 436. The Chemical Catalog Co. Inc. New York) and Harrison, Anderson, Pottinger and Lee (U.S. Bur. Fisheries, Investig. Rept. No. **40**, 1939).

Whale Oil has been produced for centuries and the history of its production forms a sequence of periods of prosperity and depression, corresponding to the discovery of new grounds, new catching methods, loss of markets through the competition of other oils, depletion of grounds, and so on. Prior to the commercial introduction of the harpoon gun in 1868 by the Norwegian whaler Svend Foyn, the oil was prepared mainly at sea aboard whale factory ships. Each ship was equipped with an open cooker (" try pot "), usually built of brick and heated by a fire fed with exhausted blubber, in which the blubber was rendered by direct heat. The whales were caught by means of hand harpoons from rowing boats, and after being killed were made fast to the side of the factory ship. There the blubber was stripped off (this process is known as " flensing ") and after recovery of any other valuable material, such as whalebone, the carcase was discarded. At the time of introduction of the harpoon gun, the whaling industry was at a low ebb, due largely to the exhaustion of the stocks of those whales which could safely be hunted in small boats. With the aid of the gun, however, and the simultaneous introduction of larger steam-driven catching vessels, the still plentiful, more active species of whale, such as blue and fin whales, became available.

The old-time factory ship accordingly disappeared and its place was taken by land factories, built at suitable sites. At these factories the whales were hauled up on to a slip and there flensed. The early blubber boilers consisted of open vessels, with open steam jets at the bottom. The blubber, cut into pieces about the size of a hand, was cooked in these for about 10–12 hours. After a further 8–10 hours standing the separated oil was run and skimmed off. The yield was poor, due largely to the presence of large pieces of insufficiently disintegrated tissue. Later, pressure cooking under 3–4 atm. was adopted and also the flesh and bones were worked up for oil by pressure cooking for long periods (12–20 hours).

Following on the discovery of the presence of large numbers of whales in the Antarctic, land stations were established in such places as S. Georgia, the S. Shetlands, Falklands, etc. However, owing partly to the large expanses of water far removed from any convenient land, factory ships once again made their appearance (about 1923), and the modern industry might be said to have become established.

The latest type of factory ship is a specially-built vessel of about 20,000 tons (sometimes much larger), complete with rendering apparatus, drying apparatus for making meal, oil purifying plant and large storage tanks. It is served by about 6 catching vessels. On the outward trip to the Antarctic (where practically all whaling is now carried out), these tanks will be partly filled with fuel oil. Supplies for land stations may also be taken, and oil from the land stations is brought back on the return trip. Tankers may also be used to bring back part of the oil. Owing to the threatened extinction of many species of whale, the industry is now strictly regulated by an international agreement (Treaty Series No. **37**, 1938, H.M. Stationery Office). Besides limiting grounds, species, size, etc., it is also laid down that the fullest possible use shall be made of all whales taken. This means, in effect, that all flesh and bones are now worked up for oil and meal.

The details of apparatus and procedure vary somewhat according to the age of the ship or land station, its nationality and any patents involved. In general, however, the principles are the same. The cooker usually consists of a horizontal cylinder inside which is a rotating perforated drum. The blubber, flesh or bones are fed into the drum through large feed-pipes which communicate with the deck above and often incorporate a pre-heating chamber. The outer casing of the cooker is provided with steam jets and an outlet pipe. Steam is admitted under a pressure of 3–4 atm. and as the perforated drum rotates, any disintegrated tissue falls through into the space below, along with oil and water. The period of cooking varies according to the material being treated, from about 1 hour for blubber to 3 or 4 hours for bones. The process is often semi-continuous, the outside of the perforated drum having a propelling worm which drives the collected oil and water towards the outlet, where it is expelled by the steam pressure in the cooker. It passes through a strainer to recover suspended solids, which are pressed and dried for meal, and then to a fat separator, which is really a specially designed settling tank. From here the crude oil is pumped off to temporary storage. It is next washed with warm seawater and passed through centrifugal oil and water separators, after which it is pumped into the main storage tanks. It is so free from water and suspended protein matter that it will not deteriorate during the months that may elapse before the ship returns to Europe.

The principal species of whales caught to-day are the blue whale (*Balaenoptera musculus*), fin whale (*B. physalus*), and humpback whale (*Megaptera boops*). The once highly important sperm whale (*Physeter macrocephalus*) is now caught only in relatively small numbers. The blue whale is the largest and a whale of 100 tons may yield 28–30 tons of oil. A fin whale gives about 8 tons of blubber oil and a humpback whale about 6·5 tons. These oils are normally mixed aboard the factory ships, but any sperm oil obtained is kept separate, in view of its entirely different composition (*vide infra*). An interesting feature of the sperm whale is that it contains a large quantity of oil in a special head cavity. This oil is liquid at the body temperature of the whale and is often obtained by simply baling it out through an opening made in the skull.

The importance of the modern industry can be judged from the fact that in the 1937/38 season, 46,039 whales were killed, yielding 557,000 tons of oil. A modern factory ship can produce up to 600 tons of oil per day, of which the greater part is of grade 1 quality.

Further details of the history and development of the whale-oil industry can be obtained from Mansbridge (J.S.C.I. 1917, **36**, 362), Kaufmann (Fette u. Seifen, 1938, **45**, 7), and Sommermeyer (*ibid.* 42). Descriptions of modern factory ship procedure and equipment are given by the last author (*l.c.*), Scholz (*ibid.* 36) and Ulrichs (*ibid.* 45). The whole of the January issue of Fette u. Seifen for 1938 is devoted to a symposium on whaling and whale oil.

CHARACTERISTICS OF FISH OILS.—Almost all fish and marine animal oils are partly solid at ordinary temperatures, the amount of "stearine" varying with the species. The colour of oil made from fresh material varies from practically colourless to golden yellow or greenish yellow (*e.g.* pilchard oil) or even red (salmon oils). Oil made from staler material is naturally much darker in colour. The percentage of free fatty acid in the crude oil depends almost entirely on the freshness of the original material from which it was made, and should be less than 2 for good quality oil. Salmon oil made from total viscera is often below this quality, however, in view of the extremely rapid autolysis in such material. Whale oil is graded into 4 grades on a basis of free fatty acid content and colour (*e.g.* the new Norwegian specification for whale oils, N.S. 487 (1939), gives the following limits : No. 1, 2% F.F.A. and 3 red Lovibond units (+35 yellow) in a 40 mm. cell; No. 2, 6% F.F.A. and 10 red units; No. 3, 15% F.F.A. and 12 red units; No. 4 anything over these).

Fish oils are normally subject to greater variation in composition than land animal or seed fats; due in part to the periods of intensive feeding and starvation which most species undergo in connection with spawning, winter food scarcity and low water-temperature, and so on. Thus the fish periodically build up fresh fat reserves and then later deplete them almost entirely. Herring, for instance, vary from about 1% of fat to over 30% and the composition of herring fat is also different at different seasons (Lovern, Biochem. J. 1938, **32**, 676). The marine mammals vary greatly in fat content during pregnancy and lactation and the fat composition varies as a result (Tveraaen and Klem, Hvalrådets Skrifter, No. **11**, 1935). The composition also varies from depot to depot, and in the case of mixed oils made from various parts of an animal (*e.g.* salmon offal oils, whale oils, etc.) the composition will vary appreciably according to the relative preponderance of one or other portion of the animal. Some commercial oils are made from several related species, *e.g.* Jap fish oil, salmon oil and whale oil, and here again variations in composition must be expected, which in many cases are quite large (Harrison, Anderson, Pottinger and Lee, U.S. Bur. Fish. Investig. Rept. No. **40**, 1939, give data for salmon oils, and Lund, Oil and Soap, 1936, **13**, 148, discusses whale oils).

It will be clear, therefore, that the characteristics normally given for a particular fat (density, refractive index, saponification value, iodine value, and so on) do not have their usual significance as a means of defining any particular fish oil. For instance, iodine values ranging from 140 to 193 have been observed with different samples of genuine menhaden oil and cod-liver oil shows similar variations (*v.* Vol. III, 246*a*). At the same time, however, it is possible to give average values for various oils, and these may vary markedly from species to species. Such variations are important commercially, as they influence the value of the oil for different purposes (*vide infra*). Actually the characteristic which shows the most variation is the iodine value. The density of most fish oils is about 0·90–0·93, the refractive index varies somewhat with the iodine value (usual limits 1·46–1·48), the % F.F.A. varies from <1 to very high values, depending entirely on the freshness of the raw material, and the unsaponifiable matter is usually <1·5% (except in the case of certain sharks and the toothed whales). The sap. val. does not vary greatly except in the case of certain sharks and the toothed whales, and normally lies between 180 and 200, most commonly about 190. The usual iodine values of the commercially important oils fall within the following limits: menhaden 160–180; sardine (Californian) about 180; sardine (Jap.) 180–190; pilchard, 175–185; herring 120–140; salmon (Pacific) 130–150; whale (baleen) 110–120; sperm whale (head oil) 50–60; sperm whale (blubber oil) 85.

Chemistry of Fish Oils. Fish and marine mammal oils differ from most land animal and seed fats in the great number of fatty acids which they contain. These normally include C_{14}, C_{16} and C_{18} saturated acids, and C_{14}, C_{16}, C_{18}, C_{20} and C_{22} unsaturated acids. Certain oils contain additional acids in greater or smaller amount, such as C_{12} or C_{20} saturated acids, C_{24} or higher unsaturated acids, and so on. The unsaturated acids contain members of varying degrees of unsaturation, ranging from mono- up to penta- and hexa-ethylenic acids. The structure of many of these acids is still uncertain, due in part to the difficulty of obtaining them in pure form and perhaps also to different workers using different species for the preparation of a particular acid. It is possible, even probable, that a C_{20} acid with, say, 4 or 5 double bonds, will not have all of these in the same positions in cod-liver oil as it has in whale oil, or sardine oil. For a description of these acids in cod-liver oil (*see* Vol. III, 247). Some additional interesting compounds include Δ^{9}-decenoic and Δ^{5}-dodecenoic acids from sperm head oil (Toyama and Tsuchiya, Bull. Chem. Soc. Japan, 1935, **10**, 570; 1936, **11**, 26; J. Chem. Soc. Japan, 1935, **56**, 1055); Δ^{5}-tetradecenoic acid in sperm blubber oil, sardine and pilot whale oils (*idem*, *ibid.* **56**, 1050; J. Soc. Chem. Ind. Japan, 1935, **38**, 680B) and hexacosapentaenoic and hexacosahexaenoic acids in tunny-liver oil (Ueno and Yonese, Bull. Chem. Soc. Japan, 1936, **11**, 437). Toyama and Tsuchiya (*ibid.* 1935, **10**, 192, 232, 241, 296, 301, 539, 547) give structural formulæ for a number of highly unsaturated acids isolated from sardine oil, ranging from a C_{16} acid with 3 double bonds to a C_{24} acid with 6 double bonds. Farmer and Webb (*see* Annual Rep. Prog. Appl. Chem. 1935, **20**, 419) postulate the presence of conjugated double bonds in certain sardine oil acids, but the work of Morrell and Davies (J. Soc. Chem. Ind. 1936, **55**, 101T) showed an absence of conjugation in the C_{20} and C_{22} polyethenoid acids of cod-liver oil. Some idea of the uncertainty and contradictory data relating to the structure of certain acids is afforded by some of the reported work on clupanodonic acid, a highly unsaturated C_{22} acid with 5 or 6 double bonds (*see* Armstrong and Hilditch, J. Soc. Chem. Ind. 1925, **44**, 180T; Tsujimoto, Bull. Chem. Soc. Japan, 1928, **3**, 299; Toyama and Tsuchiya, *ibid.* 1935, **10**, 301; Inoue and Sahashi, Proc. Imp. Acad. Tokyo, 1934, **10**, 463; Kino, Sci. Papers Ins. Phys. Chem. Res. Tokyo, 1934, **24**, 218; Farmer and Van den Heuvel, J. Chem. Soc. 1938, 427). Further references to the acids occurring in fish oils can be found in the Annual Rept. Progress Appl. Chem.

In the great majority of fish oils these acids are combined as mixed triglycerides. The number of possible combinations is obviously very great, and it is not surprising that no quantitative separation and estimation of individual glycerides has been found possible. Suzuki and co-workers (Proc. Imp. Acad. Tokyo, 1927, **3**, 531; 1928, **4**, 165; 1931, **7**, 9), by means of selective crystallisation of brominated oils, have established the presence of numerous mixed glycerides in various fish oils. Using an entirely different technique involving partial hydrogenation, Hilditch and his co-workers have reported on the glyceride structure of Antarctic whale-oil and a North Sea cod-liver oil (J. Soc. Chem. Ind. 1937, **56**, 310T). In certain sharks much of the total fatty acids is combined with glyceryl ethers of higher aliphatic alcohols (*vide infra*), whilst in the fats of the toothed whales much of the acids is present as wax esters of higher aliphatic alcohols, instead of as glycerides. Hilditch and Lovern (J.S.C.I. 1929, **48**, 359T) have reported on the general structure of sperm-head and blubber oils. Tsujimoto and his co-workers have employed vacuum distillation of various toothed-whale oils as a means of separating the wax fractions from the less volatile triglycerides (J. Soc. Chem. Ind. Japan, 1937, **40**, 191B, 272B, 315B, 403B; 1938, **41**, 41B). Lovern (Biochem. J. 1934, **28**, 394) has given data on the structure of a porpoise-body fat.

The methods available for the analytical examination of fish oils are in the main those applying to fats in general. With such a complex mixture of fatty acids it is not possible to effect a quantitative separation of all the acids and the usual way of reporting a fatty acid composition is by means of groups, as illustrated in Vol. III, 247 Table II. It is possible, however, by means of lithium fatty-acid salt/acetone separation, bromination and similar means to separate the more highly-unsaturated members of a group from less unsaturated acids of the same number of carbon atoms, and this technique is sometimes adopted. Details of the usual procedure (involving lead salt/alcohol separation of the fatty acids, esterification, fractional distillation under reduced pressure, oxidation of certain fractions and calculation of the composition of each fraction from its iodine value and saponification equivalent) are given by Guha, Hilditch and Lovern (Biochem. J. 1930, **24**, 266), Hilditch (Fette u. Seifen, 1936, **43**, 97), and Harper, Hilditch and Terleski (J. Soc. Chem. Ind. 1937, **56**, 310T). Charnley (Contrib. Canad. Biol. Fish. 1934, **8**, 509) has discussed the calculations involved.

A sufficient number of fish oils have now been analysed by this means to enable a number of generalisations to be made. The majority of species have fatty acid compositions not very different from those given for cod-liver oil (*q.v.*) and related oils. At the same time, however, there is a noteworthy tendency for the oils to fall into groups of even more closely similar compositions, and such groups are normally composed of species related zoologically. Hilditch and Lovern (Nature, 1936, **137**, 478) have discussed the significance of this phenomenon, which applies to the whole field of fats. Freshwater species, as a whole, have a characteristically higher content of C_{18} unsaturated acids and a lower content of C_{20} and C_{22} unsaturated acids than marine species (Lovern, Biochem. J. 1937, **31**, 755).

In contrast to this general type of fish oil (which includes the oils from baleen whales), certain species have fats differing sharply from such a type. The principal species involved are certain sharks and the toothed whales. The oils of many varieties of shark are fairly normal, but in others the fatty composition differs in that the acids tend to be considerably less unsaturated than usual and that unusually large amounts of C_{24} acids are present (in most fish oils C_{24} acids are either absent or present only in traces). Concurrently with this much of the glycerol of the oils is replaced by monoglyceryl ethers of hexadecyl, octadecyl and octadecenyl alcohols (chimyl, batyl and selachyl alcohols). In certain cases large amounts of the highly-unsaturated, branched chain hydrocarbon squalene are present (Tsujimoto, J.S.C.I. 1932, **51**, 317T; J. Soc. Chem. Ind. Japan, 1935, **38**, 271B, 272B; 1936, **39**, 82B; 1937, **40**, 365B; Hilditch and Houlbrooke, Analyst, 1928, **53**, 246; T. P. Hilditch, " Chemical Constitution of Natural Fats," Chapman and Hall, London, 1940).

The depot fats of the toothed whales (sperm whale, bottlenose whale, dolphins, porpoises, etc.) are noteworthy for the relative saturation of their fatty acids, the presence of acids of lower molecular weights than usual and the replacement of much of the glycerol by higher aliphatic alcohols (both saturated and unsaturated). The porpoise and dolphin fats are unique in containing *iso*valeric acid, which is combined as an integral part of the fat (Lovern, Biochem. J. 1934, **28**, 394; Tsujimoto and Koyanagi, J. Soc. Chem. Ind. Japan, 1937, **40**, 272B). The alcohols occurring in toothed-whale fats are mainly tetradecyl, hexadecyl, octadecyl, hexadecenyl, octadecenyl and eicosenyl alcohols. Hilditch and Lovern (J.S.C.I. 1929, **48**, 365T; 1933, **52**, 90T) give the quantitative composition of the alcohol mixtures occurring in sperm-head and blubber oils. In addition, however, traces of the following alcohols have been reported: octyl, decyl and dodecyl alcohols, unsaturated C_{10} and C_{11} alcohols (Ueno and Koyama, J. Chem. Soc. Japan, 1936, **57**, 1; Bull. Chem. Soc. Japan, 1936, **11**, 394); tetradecenol, eicosatetraenol and docosapentaenol (Toyama and Tsuchiya, Bull. Chem. Soc. Japan, 1935, **10**, 572; Toyama and Akiyama, *ibid.* 579; 1936, **11**, 29).

Whilst these alcohols and alcohol-ethers will appear in the unsaponifiable fraction of the fat, it should be remembered that they are really present as saponifiable esters and merely take the place of glycerin in a normal fat. Squalene (and other hydrocarbons present in some shark oils) is, however, true unsaponifiable matter.

The above survey of the chemical composition of aquatic animal fats has necessarily been brief and is far from being complete. It will serve, however, to give a general idea of the type of compounds occurring in such fats and illustrate the difference between them and the usual land animal and seed fats. For fuller information on the chemistry of fish oils, *see* the " Oils, Fats and Waxes " section of the Annual Rep. Prog. Appl. Chem.; Hilditch (Proc. 5th Pacific Sci. Congr. Victoria and Vancouver, B.C., Canada, 1933, 3647) and Lovern (Biochem. J. 1932, **26**, 1978, 1985; 1934, **28**, 394, 1955, 1961; 1935, **29**, 1894; 1936, **30**, 2023; 1937, **31**, 755; 1938, **32**, 1214).

In Table I are given the fatty acid compositions of a few representative fish oils, including most of the commercially important species. The three shark oils have been selected to illustrate the fairly normal type, the relatively saturated type and an intermediate type. The toothed-whale fats illustrate not only the peculiar composition of such fats, but also the different compositions of fats from different depots in the same animal. This point is an important one, as the same is often true of many other species. As an example of the extreme differences that may be encountered it may be mentioned that the liver and organ fats of the sperm whale and porpoise closely resemble fats of the cod-liver oil type and have no lower acids and no wax esters (Tsujimoto and Kimura, Chem. Umschau, 1928, **35**, 317; Lovern, Biochem. J. 1934, **28**, 394). It has already been mentioned that fish oil compositions are subject to considerable variation, but the data given in Table I will serve to give a general idea of the types of fatty-acid mixture occurring in these oils.

Refining of Fish Oils.—It has been mentioned that raw fish-oils are normally partly solid at ordinary temperatures, and of varying colour from practically colourless to reddish yellow. Oils from somewhat stale material may be brown in colour and have a relatively high content of free fatty acid and a strong odour. The refining necessary before an oil is suitable for an industrial use depends mainly on the particular purpose to which it is to be put, for some purposes no refining at all being necessary. The following refining processes are in use: wintering, alkali-refining, decolorising and deodorising.

Wintering consists in removal of stearin by cooling the oil, allowing the stearin to settle out and then removing it in a filter press. The purified oil will be quite liquid at ordinary temperatures and the process also removes any traces of water and mucilage in the crude oil. The temperature to which the oil is cooled will depend on the nature of the oil and the purpose to which it is to be put and the cooling should always be done gradually as the separation of stearin is a very slow process.

Alkali-refining for the purpose of removing free fatty acid, is carried out just as for vegetable fats, etc., by stirring the oil with the required amount of caustic soda solution. A certain amount of colouring matter is removed at the same time. The purified oil is run off from the settled " foots."

TABLE I.—PERCENTAGE COMPOSITION OF THE FATTY ACIDS OF AQUATIC ANIMAL FATS.

Type and species.	Depot.	Saturated.						Unsaturated.						
		C_5	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}
FRESHWATER FISH														
Carp [1] . . . . (*Cyprinus carpio*)	Flesh . .	—	—	—	3·7	14·6	1·9	—	1·0	17·8	45·8 (−3·2H)	15·2 (−6·9H)	—	—
Perch [1] . . . . (*Perca fluviatilis*)	Flesh . .	—	—	—	3·5	12·5	2·0	—	1·1	19·4	40·5 (−3·2H)	13·8 (−6·8H)	7·1 (−9·2H)	—
SEA FISH *														
Herring family—														
Herring [2] . . . . (*Clupea harengus*)	Flesh . .	—	—	—	8·3	12·1	0·3	—	0·5	6·4 (−3·4H)	21·0 (−4·5H)	28·3 (−5·5H)	23·1 (−4·6H)	—
Menhaden [3] . . . . (*Brevoortia tyrannus*)	Whole fish .	—	—	—	6	16	1·5	—	—	15·5	30	19	12	—
Jap. Sardine [3] . . . . . . (*Clupanodon melanostocta*)	Whole fish .	—	—	—	6	10	2	—	—	13	24	26	19	—
Pilchard [4] . . . . (*Sardinops cærulea*)	Whole fish .	—	—	—	5·1	14·4	3·2	—	0·1 (−2·0H)	11·8 (−2·0H)	17·7 (−3·3H)	17·9 (−4·1H)	13·8 (−8·5H)	15·2 (−10·9H)
Sharks—														
Thresher shark [5] . . . . . . (*Alopoecia vulpes*)	Liver . .	—	—	—	7·4	11·3	0·2	—	1·6	12·0 (−2·0H)	19·2 (−3·4H)	31·0 (−6·6H)	17·3 (−10·5H)	—
Dogfish [6] . . . . (*Squalus acanthias*)	Liver . .	—	—	—	6	10·5	3	—	—	9 (−2·0H)	24·5 (−2·3H)	29 (−3·3H)	12 (−4·0H)	6 (−2·0H)
Scymnorhinus lichia [7]	Liver . .	—	—	—	1	14·5	3·5	—	0·5	4	29	10·5 (−2·0H)	26 (−2·0H)	10 (−2·0H)
Whales—														
Mixed Antarctic [8]	Mainly blubber.	—	—	—	7·5	19·3	2·3	—	4·4 (−2·0H)	14·2 (−2·0H)	37·0 (−2·6H)	10·1 (−5·6H)	5·2 (−9·0H)	—
Sperm whale [9] . . . . (*Physeter macrocephalus*)	Head . .	—	3·5	16	14	8	2	4	14	15	17 (−2·0H)	6·5 (−2·0H)	—	—
Ditto	Blubber .	—	—	1	5	6·5	trace	—	4	26·5	37 (−2·1H)	19 (−2·6H)	1 (−3·6H)	—
Porpoise [10] . . . . (*Phocaena communis*)	Jaw . . .	25·3	—	4·6	28·3	4·1	—	—	3·2	20·3	9·3 (−2·6H)	4·9 (−4·9H)	—	—
Ditto	Body blubber	13·6	—	3·5	12·1	4·7	—	—	4·7	27·2	16·7 (−2·8H)	10·5 (−4·8H)	7·0 (−4·9H)	—

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* For the cod family, *see* Cod-Liver Oil.

[1] Lovern, Biochem. J. 1932, **26**, 1978.

[2] Lovern, *ibid.* 1938, **32**, 676.

[3] Armstrong and Allen, J.S.C.I. 1924, **43**, 216T.

[4] Brocklesby and Harding, J. Fish. Res. Board, Canada, 1938, **4**, 59.

[5] Lovern, Biochem. J. 1930, **24**, 866.

[6] Guha, Hilditch and Lovern, *ibid.* 266.

[7] Hilditch and Houlbrooke, Analyst, 1928, **53**, 246.

[8] Hilditch and Terleski, J.S.C.I. 1937, **56**, 315T.

[9] Hilditch and Lovern, *ibid.* 1928, **47**, 105T.

[10] Lovern, Biochem. J. 1934, **28**, 394.

Decolorising is usually carried out by agitating the heated oil with an adsorbent earth (fuller's earth, etc.), or a mixture of earth and charcoal. About 5% of earth is used and bleaching occupies about 15–30 minutes. The earth is then removed in a filter press.

Deodorising can be accomplished by blowing with superheated steam in a vacuum, in the usual way. Care must be taken to use as low a temperature as possible to avoid polymerisation of the more highly unsaturated glycerides.

Uses of Fish Oils.—For many purposes the various fish oils of commerce are interchangeable, whilst for others certain oils are preferred, *e.g.* the more highly unsaturated oils for paint manufacture and the less highly unsaturated ones for margarine manufacture. The principal uses to which fish oils are put are dealt with only briefly here, as fuller information can be obtained under the appropriate heading elsewhere in this Dictionary.

Fish Oils as Sources of Vitamins A and D.—The best-known sources of these vitamins for both human and animal requirements are cod- and other fish-liver oils (*v.* Vol. III, 250). Several of the non-liver oils of commerce, however, are being increasingly used as a vitamin supplement in animal nutrition. Oils made from whole fish of the herring family, such as herring, menhaden, sardine and pilchard are quite good sources of vitamin D, but in general have only a low vitamin A content. Salmon offal oils are good sources of both these vitamins. Morgan, Kimmel and Davison (Food Research, 1939, **4**, 145) report that Pacific sardine oils contain from 35–95 U.S.P. units of vitamin D per gram, one sample having 100 U.S.P. units/g. The vitamin A content was usually low, but many of the oils were thus at least equal to the U.S.P. reference cod-liver oil (85 units/g.) in vitamin D content (*see also* Asmundson and Allardyce, Sci. Agric. 1933, **13**, 749; Biely and Palmer, *ibid.* **14**, 136). Pilchard oil contains from 20 to 100 I.U./g. of vitamin D (varying seasonally) and sometimes appreciable amounts of vitamin A (Bailey, Biol. Board Canada Prog. Rep. Pacific, 1935, No. **23**, 11; Brocklesby, *ibid.* No. **25**, 13; Pugsley, Fish. Res. Board, Canada Prog. Rep. Pacific, 1939, No. **39**, 3; Asmundson and Allardyce, *l.c.*; Biely and Palmer, *l.c.*; Biely and Chalmers, Proc. World's Poultry Congr. 6th Congr. Berlin and Leipzig, 1936, Sect. 2, 228; Milne, Rudolph and McFarlane, Poultry Sci. 1937, **16**, 383). Herring-body oil (Pugsley, Fish. Res. Board Canada Prog. Rep. Pacific, 1938, No. **35**, 7; No. **38**, 7; Lunde, Nord. Med. Tids. 1938, **15**, 444; Angew. Chem. 1939, **52**, 521) and menhaden oil (Manning, Nelson and Tolle, U.S. Bur. Fish. Invest. Rep. 1931, No. **3**; Halverson, Smith, Sherwood, and Dearstyne, N. Carolina Agric. Expt. Sta. Tech. Bull. **57**, 1938) are equal to cod liver oil in vitamin D. Morgan, Kimmel and Davison (*l.c.*) report that samples of commercial salmon-offal oils contained 58–142 units/g. of vitamin D and that some of them approached the minimum vitamin A standard of the U.S.P. cod-liver oil. Harrison, Anderson, Holmes and Pigott (U.S. Bur. Fish. Invest. Rep. 1937, No. **36**) also give data for the vitamin content of salmon oils, showing wide variations from species to species (especially for vitamin A). Some oils were superior to good cod-liver oil as sources of vitamin A, others were superior in vitamin D. Sockeye and silver salmon oils are good sources of both (*see also* Harrison, Anderson, Pottinger and Lee, *ibid.* 1939, No. **40**).

All these oils seem to be especially used in poultry feeding and either the crude or "wintered" oils are employed. Oils intended for such purposes should be made by processes involving as little prolonged heating as possible, and centrifugal separation is, therefore, preferable to a settling tank system (Harrison and Pottinger, *ibid.* 1931, No. **4**; Brocklesby and Bailey, Biol. Board Canada Bull. 1935 No. **46**,). Whale oils do not seem to be used as a vitamin supplement, but whale-liver oil is a valuable commercial source of vitamin A (Bomskov and Unger, Fette u. Seifen, 1938, **45**, 90).

Fish Oils as Source of Edible Fats.—Any good quality fish oil, with the exception of oils from toothed whales and certain sharks, may be converted into an edible fat by suitable hydrogenation. The treatment involves alkali-refining if necessary (free fatty acid attacks the reaction vessel and the other impurities removed during alkali-refining, slimy matter, phosphatides, etc., are catalyst poisons) and bleaching with fuller's earth. The extent of the hydrogeneration depends on the particular product being manufactured and on the composition and degree of unsaturation of the original oil. Oils of equal iodine value do not necessarily have the same melting-point and in fact fish oils, with their mixture of acids of various molecular weights, give a product which melts over a considerable range instead of sharply. This is a favourable quality in such a fat as margarine, for example, as it confers increased plasticity. The hydrogenated edible fats of commerce are usually blended products rather than entirely made from fish oils, and obviously the degree of hardening of the fish oil will also depend on the other fats with which it is to be mixed. The hydrogenation process is often controlled in such a manner as to produce the maximum content of *iso*-acids (unsaturated acids in which a double bond has changed its position), which are especially valuable in connection with plasticity. This control can be exercised by using a somewhat dull catalyst and relatively high temperatures. For making solid fats, such as lard substitutes and margarine, a fish oil of relatively low iodine value is preferable, as less hydrogen will be required. Such oils will include pre-eminently whale oil (I.V. about 120) and fish-oil stearins separated in the wintering of other oils. Incidentally, whale oil was the first fat to be hardened on a full factory scale for use as a foodstuff (in 1910). Oils for lard substitutes are not so fully hydrogenated as those for margarine. A certain amount of fish oil of high iodine value is slightly hydrogenated to furnish liquid cooking fats for frying purposes.

The hydrogenated products have lost entirely all fishy flavour but acquire during the process a characteristic odour, which is removed by blowing with steam.

A historical account of the development of the hydrogenation of whale oil for margarine manufacture, with details of procedure, is given by Normann (Fette u. Seifen, 1938, **45**, 73). Additional information can be obtained from Brocklesby and Denstedt (Biol. Board Canada Bull. No. **37**, 1933).

Fish Oils in Soap and Detergent Manufacture.—Untreated fish oils are rarely used in soap manufacture (except in certain soft soaps) since the product has an objectionable odour, is dark in colour and does not keep well owing to the rapid onset of rancidity. Partly hydrogenated oils, however, have excellent soap-making qualities and the wide range of acids is an advantage in that the resulting soap has suitable emulsifying and lathering properties over a considerable temperature-range. Careful control of the hydrogenation process is necessary to ensure a good soap-making fat. Another method of removing the highly-unsaturated acids, which are undesirable for soap manufacture, is by heat polymerisation of the oil, and, in fact, this method was in use in the soap industry long before hydrogenation processes had been discovered. A combination of sulphonation and polymerisation, followed by saponification, gives a soap of unusual emulsifying power and solubility (even in brine), and such products made from fish oils are widely incorporated in household and other soaps.

In the superfatting of certain soaps (especially toilet soaps) common superfatting agents include wax alcohols and spermaceti (Glenn, Soap, 1939, **15**, 21). Spermaceti is the solid fraction recovered by cold-pressing sperm-head (and to a lesser extent sperm-blubber) oils and sperm oils are also a valuable source of wax alcohols.

Modern developments in the manufacture of soapless detergents commonly require wax alcohols as raw materials. These are sulphated and the acid sulphates converted into sodium salts, etc., giving products of great emulsifying power and high solubility. Sperm oils can readily be converted into wax alcohols by high pressure hydrogenation (about 200 atm.), and the yield is somewhat greater than with ordinary glyceride oils, whilst the hydrogen consumption is less.

Details of the use of fish oils in soap manufacture are given by Lindner (Fette u. Seifen, 1938, **45**, 76) and Brocklesby (Biol. Board Canada Bull. No. **37**, 1933).

Fish Oils in Paints, Linoleum, Waterproofing, etc.—Fish oils, especially the more unsaturated ones, find considerable application as sources of drying oils, for use in the paint, varnish and allied trades. For the general treatment of this subject (*see* Drying Oils).

Fish Oils in the Leather Trade.—Fish oils find extensive use in the leather trade, both as tanning agents (in chamoising) and for impregnating leathers to confer, among others, such qualities as flexibility and impermeability to water. In addition sulphonated fish oils are widely used as emulsifying agents in such impregnation processes. In the chamoising process the exact mechanism of tanning is still uncertain, but an essential feature is the oxidation of the poly-unsaturated acids of the fish oil and the combination of the products with the protein of the sheep skins. The principal fish oil used in the leather trade is cod oil (low grade cod-liver oil), but other fish oils, including whale oil, are also used, especially on the Continent. Stather (Fette u. Seifen, 1938, **45**, 86) discusses the uses of whale oil in this industry.

Miscellaneous Uses of Fish Oils.—Among the minor industrial uses of fish oils must be included the manufacture of lubricants, cutting oils, candles, cosmetics and pharmaceutical products. In former days considerable quantities of certain fish oils (notably whale oil and sperm-whale oil) were used as lubricants, but the gumming tendency of most of such oils (due to oxidation) is a great drawback. Hydrogenated fish oils and fish-oil stearins are used as ingredients of greases and other solid lubricants, and sperm oil (the liquid fraction from the crude oil) is still used for certain purposes, notably for *machine oils* for light machinery and clockwork. The head and jaw oils of porpoises and dolphins are claimed to be the ideal lubricant for delicate machinery, but the supply is very limited and uncertain and the price is high.

Cutting oils are the oils used as lubricants in the machining of metal. They usually contain sulphonated or sulphurised fish-oil as an emulsifying agent.

Candles nowadays consist largely of paraffin wax, but at one time tallow and spermaceti candles were in common use. The standard candle used as a measure of light intensity is a sperm candle. Even to-day many candles contain a proportion of spermaceti or fully hydrogenated fish-oil or the acids from such an oil. Von Krueger (Fette u. Seifen, 1938, **45**, 81) gives an account of the use of fish-oil products in candle manufacture and as illuminants in general.

Spermaceti and higher aliphatic alcohols such as cetyl alcohol (often commercially derived from sperm-whale oil) are used in cosmetics especially as ingredients of face creams, salves, grease paints, lipstick and nail wax. Cetyl alcohol is often incorporated in shaving creams. A full account of such uses is given by Filmer (*ibid.* 105). Spermaceti and cetyl alcohol also find a use in pharmacy, principally in ointments (*see* Kaufmann, *ibid.* 94).

Other minor industrial uses of fish oils, which in the aggregate furnish a considerable outlet for these products, include the manufacture of artificial leather, use as an adhesive in insecticide sprays, use in the compounding of rubber and rubber substitutes, printers' ink, floor and furniture polishes and artificial resins.

J. A. L.

FISKE'S EXTRACTOR (*v.* Vol. IV, 586*c*).

FLAGSTONE. A stratified rock which may be split along the planes of bedding into smooth-faced slabs, suitable for use as paving stones. If the stone is too absorbent, or finely laminated, the surface is apt to flake off by the action of frost. As hardness and durability are essential in a flagstone, sandstones are superior to calcareous or argillaceous rocks. The flaggy sandstones are generally micaceous; and their fissility may be partly due to the presence of mica along definite planes. The best English flagstones are derived from the lower Coal-Measures, the Millstone Grit and the Yoredale rocks. Most of the flags used for paving the streets of London are obtained from the Yorkshire coalfield. The Elland flagstone, which is extensively worked, is a fine-grained micaceous sandstone from the lower Coal-Measures, or ganister series, extending with persistence through the coalfields of Yorkshire, Lancashire and Derbyshire. In Scotland, the lower Old Red Sandstone yields paving slabs of very large size, the best known being the dark-grey flagstones of Caithness and the Arbroath pavement of Forfarshire. The celebrated Caithness flagstone is one of the most important economic products of the Old Red Sandstone. It is used locally as a building stone, and for use as stone flooring and staircases it has been exported to all parts of the world. The extensive works for Liebig's meat-extract on the River Plate in South America are floored throughout with Caithness flags. The stone is finely laminated, tough and compact, and its cementing material is siliceous, argillaceous, calcareous and bituminous. The last of these, derived from the vast number of fossil fishes, renders the stone impervious to moisture. Analysis of stone from the Castle Hill quarries at Thurso, Caithness-shire, gave: SiO_2, 69·45; $Al_2O_3+Fe_2O_2$, 10·50; K_2O+Na_2O, 2·20; $CaCO_3$, 10·65; organic matter, 5·79%. Weight per cubic foot, 157 lb.

L. J. S.

FLAKE or PEARL WHITE (*v.* Vol. I, 699*d*).

FLAME. Although mankind has known the use of fire from very early times the precise definition of "flame" is a problem of some nicety. Davy who gave a rational basis to the science of the subject described a flame as "gaseous matter heated to such a degree as to be luminous." Generally speaking, however, common gases will not glow as a result of simple heating at any rate up to say 2,000°C. Iodine vapour glows at a red heat but this is ascribed to dissociation of the molecules. In flame production, chemical reaction causes heating and luminosity, but hydrogen and air can burn under conditions such that the flame is scarcely visible even in the dark. There is an emission of radiation but outside the visible spectrum. For practical purposes a flame is glowing gas, the glow being the accompaniment of chemical change. This definition includes phosphorescent flames which may be quite cool in comparison with the normal hot flame, and also the so-called "cool flames."

The use of the word "luminous" as a characteristic of flame needs qualification because in practice it is common to distinguish between non-luminous and "luminous flames" whereas all in some degree glow. The so-called "luminous flames" are characterised by the presence in the flame of suspended particles. These hot particles have an emissive power greatly exceeding that of the tenuous gaseous medium in which they are immersed and so greatly increase the visible radiation from the flame as to justify a distinction from the relatively feebly glowing flame in which no solid particles are present.

A flame may be produced when chemical reaction occurs between gases or with the production of gas provided that the liberation of energy is adequate. The liberation of heat accompanying flame is usually considerable. Examples are the exothermic union of CO and oxygen to form CO_2 or of hydrogen atoms to form molecules, the exothermic decomposition into gaseous constituents of explosives such as guncotton, or of endothermic compounds such as acetylene into its elements. In phosphorescent flames such as that of phosphorus, the energy liberated per gram molecule is quite considerable.

In recent years it has been found that "cool flames" may be propagated under certain conditions of temperature and pressure. The conditions are low-pressure and defective proportions of oxygen at temperatures sufficing to initiate reaction but to permit the formation of intermediate products of oxidation only. The reaction is accompanied by characteristic blue or green glows, but in general no high temperature unless, as in some cases, the "cool flame" may be transformed into an ordinary flame. (*See* EXPLOSIONS, GASEOUS, Vol. IV, pp. 419 *et seq.*)

It might be supposed that the chemistry of flames would be simple as the reactions often involve matter in its simplest form, and the reactions themselves are often of the simplest type. This appearance of simplicity is illusory. The reactions are so extremely rapid and intense that the course of the transformation of chemical into kinetic energy of the gaseous products is still largely conjectural, for it cannot be followed by normal chemical analysis and the study demands the newest and most searching efforts of modern chemistry and physics.

In the region of temperature below but not too far below the ignition temperature where oxidation proceeds at a moderate and controllable rate it is possible to examine the progress of combustion by chemical methods. Thus Bone accumulated evidence to show the gradual oxidation of hydrocarbons by stepwise hydroxylation (Bone and Townend, "Flame and Combustion in Gases," Longmans Green, 1927).

The subject has been developed by the application of the theory of reaction chains. For an account of the extensive literature, *see* Semenoff, "Chemical Kinetics and Chain Reactions," Oxford Press, 1935; Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, 1926 and 1940; Lewis and von Elbe, "Combustion, Flame and Explosions of Gases," Cambridge University Press, 1938, and EXPLOSIONS, GASEOUS, *l.c.*

Flames produced in the decomposition of single endothermic substances have a certain interest. In the case of acetylene, it is of practical importance for, while at atmospheric pressure the process is feeble, at higher pressures, *e.g.* over 2 atmospheres, the decomposition can be dangerously explosive. In practice, the important flames are those produced by the reaction of a combustible substance with oxygen—usually in air—and unless otherwise stated will be the subject of discussion in this article. For flames in closed vessels and detonations, *see* EXPLOSIONS, GASEOUS, Vol. IV, 434 *et seq.*

CONDITIONS DETERMINING FLAME.—Before a flame can be produced, a so-called "inflammable" material and oxygen must be brought together within certain limits of proportion dependent on the nature of the material in question and the conditions obtaining. An inflammable substance does not inflame until it has become mixed with oxygen and ignited. In spite of the efforts of generations of experimenters obscurity surrounds these phenomena and in particular the influence of water vapour which Dixon showed to be essential, even in extremely minute quantities, to the initiation of the combustion of carbon monoxide and oxygen.

Open flames of carbon monoxide with air or oxygen are influenced by quite moderate degrees of drying. On the other hand no attainable degree of drying cyanogen and oxygen sufficed to prevent explosion. Bone and Weston (Proc. Roy. Soc. 1926, A. **110**, 615) have shown that a carbon monoxide—oxygen mixture dried over P_2O_5 for 2 years could be ignited by sufficiently powerful sparks.

LIMITS OF INFLAMMABILITY.—Mixtures of two gases such as hydrogen and oxygen will not inflame if there be either too little hydrogen or too little oxygen present to produce on combustion sufficient heat to ignite the adjacent unburnt mixture. It is necessary therefore to distinguish between "Lower" and "Upper" limits of inflammability (referring to the percentage of the so-called inflammable gas) between which limits all mixtures are capable of burning. These limits, however, are not precise numbers but depend on conditions. As the limit is dependent on the existence of a local sufficiency of heat, anything which serves to drain heat from the system will interfere with the propagation of flame, and may even extinguish a flame once started. If the mixture is confined in a small tube, the limits may depend on the diameter of the tube and the thermal conductivity of the material. In an extreme case such as exhibited by small tubes of metal or metal gauze, propagation of the flame may be entirely suppressed—as exemplified by the miner's safety lamp. When a mixture is confined in a tube, the limits may be wider if the gas is ignited at the bottom than if ignited at the top. Again the method of ignition has a considerable influence.

For all these reasons the results given in the literature show considerable divergence. Where it is a question of safety and volumes are large, the widest possible limit should be adopted. Coward estimated that the lowest limits for the three commonest fuel gases burning with air were: hydrogen 4·1%, methane 5·3%, carbon monoxide 12·5%.

Very low concentrations of gases and vapours of high calorific value will give inflammable mixtures. Limits are often widened at higher temperatures and pressures.

Le Chatelier propounded the rule that when 2 limit mixtures (both upper or both lower) are mixed, the resulting complex mixture will itself be a limit mixture.

A set of comparative figures for gas/air mixtures burning upwards in tubes 7·5 cm. in diameter is as follows:

	Lower.	Upper Limit.
	%	%
Hydrogen	4·1	75
Carbon monoxide . .	12·8	72
Methane	5·35	14·85
Pentane	1·42	8·0
Ethylene	3·02	3·40
Acetylene	2·60	80·5
Benzene	1·41	7·45
Carbon disulphide . .	1·06	50·0

Coward and also White have confirmed the validity of this rule more particularly for "lower" limit mixtures as shown by the following figures:

	Lower.	Upper.
	%	%
Coal gas	5·35 (5·36 calc.)	30·9 (28·8 calc.)
Water gas, 50 $CO/50$ H_2	6·05 (6·2 calc.)	71·8 (72·5 calc.)

A comprehensive compilation of data of limits of inflammability is given in Bone and Townend, *op. cit.*

Temperature of Ignition.

The temperature of ignition may be defined as the temperature to which a gaseous mixture must be heated to produce a self-sustaining flame. As this depends on the rate of a chemical reaction, it is clear that ignition temperatures will be influenced by all the factors on which reaction velocities depend, and it is not surprising that the figures obtained by different observers vary widely according to the method used. Moreover, particular interest attaches to the phenomena observed when gaseous combustible mixtures are heated to temperatures

THE IGNITION TEMPERATURES OF GASES.

	Ignition temperature, °C.			
	In oxygen.		In air.	
	Between.	Mean.	Between.	Mean.
Hydrogen .	580–590	585	580–590	585
Carbon monoxide (moist)	637–658	650	644–658	651
Cyanogen .	803–818	811	850–862	856
Ethylene .	500–519	510	542–547	543
Acetylene .	416–440	428	406–440	429
Hydrogen sulphide . .	220–235	227	346–379	364
Methane .	556–700	—	650–750	—
Ethane . .	520–630	—	520–630	—
Propane . .	490–570	—	—	—
Ammonia .	700–800	—	—	—

near but below those at which flame propagation takes place, as set out in Explosions, Gaseous, Vol. IV, pp. 419 *et seq.*

The measurements of Dixon and Coward (J.C.S. 1909, **95**, 514) indicate the comparative ignition temperatures of common fuel gases with air and oxygen. The gases were heated separately to the same temperature before meeting and the temperature when inflammation was observed was noted.

When ignition is effected by contact with hot surfaces, their condition is of great importance as indicated by the diversity of figures recorded. An extreme example is given by the observation of W. Davies (Phil. Mag. 1935, **19**, 309) that an explosive mixture of CO and air is not ignited by contact with a platinum wire at 1,200°, although ignition occurs at higher and lower temperatures. Thus, finely divided platinum at air temperature may accelerate the union of oxygen and hydrogen to such an extent as to cause a mixture of coal gas and air at air temperature to ignite. This device is used commercially for the ignition of gas burners (L. W. Andrew, A. B. Densham and E. W. Voice, Trans. Inst. Gas Eng. 1937–38, **87**, Comm. No. 174, 474).

Similarly, spark ignition is influenced by the size and character of the spark.

Types of Flame.

A stationary flame may be produced by igniting an inflammable mixture as it issues into a neutral atmosphere, or by allowing one of the combining gases to issue from an orifice into an atmosphere of the other, and igniting the self-made mixture at the orifice. A third method is to allow a mixture with one gas in excess to issue into an atmosphere containing the other. All these conditions are found in practice, and they merge into each other. A flame of carbon monoxide in air lends itself readily to experimental demonstration (Fig. 1).

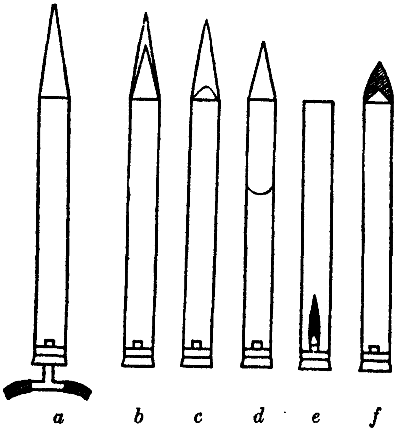

Fig. 1.

If undiluted carbon monoxide be delivered from a cylindrical tube under a gentle pressure into a still atmosphere of air, the flame which is formed appears to be a simple hollow blue cone resting upon the orifice of the tube (*a*). There is a perceptible gap of extinction between the end of the tube and the superimposed flame. A finite interval of time is necessary before the gas finds sufficient air to make an inflammable mixture and for this mixture to be ignited.

The escaping gas makes its own mixture by interdiffusion with the surrounding air ("secondary air") and so the stream is burnt through from the periphery to the central axis as the gas ascends. The central core of gas must rise some distance before reaching a supply of unconsumed air and consequently the shell of burning gas takes a pointed shape, described as a "cone." When the velocity of issue is increased, the stream becomes more turbulent and the shape of the flame increasingly disordered. The combustion is determined by interdiffusion of carbon monoxide and air.

The addition of a small quantity of air ("primary air") to the carbon monoxide before it issues from the orifice produces a noticeable effect upon the flame. The cone diminishes in height and seems to have a lining of brighter blue (*b*). With a little more air, the lining is seen to be a second cone within the first and consequently with a gentler slope. The individuality of this inner cone becomes apparent when the proportion of primary air mixed with the issuing gas is sufficient to bring the mixture well within the limits of "inflammability" (*c*). The mixture is, indeed, inflaming downwards, but as the rate of propagation does not exceed the upward velocity of the gas stream, the inner cone of flame cannot travel against the gas stream. With more air, however, a greater rate of inflammation ensues and eventually the inner cone, after becoming more and more squat, enters the tube and travels against the gas stream, first as a flat disc and then as a convex surface with the bulge downwards (*d*). Throughout all these changes, the second or outer cone is maintained at the orifice of the tube by the combustion, in the external air, of the carbon monoxide in excess of that which the primary air suffices to oxidise in the inner cone or disc. It loses in brilliance owing to its dilution with the carbon dioxide and nitrogen which come from the inner cone. If the primary air supply be increased until it can complete the oxidation of the carbon monoxide, the outer cone will disappear altogether (*e*). This, however, is not the end point, for an excess of primary air just like a defect diminishes the rate of inflammation, and consequently when the rate has been reduced below the velocity of the outflow of the gaseous mixture the single (inner) cone of flame will rise again to the orifice of the tube and remain there. It is to be noted that now the flame consists of only one film of burning gas. The film is still conical, but it has considerable thickness and its lower boundary is also a conical surface (*f*). The term "solid" has been used to distinguish a flame of gas which is burning continuously throughout the whole or nearly the whole space included by its external surface from one which is burning in thin films and whose external surface includes chiefly unburned gas; but a "solid" carbon monoxide flame is obviously a contradiction in terms, and the two types of flame might be more suitably designated as " volume " and " film " flame respectively.

The last stage to be described in the development of the carbon monoxide/air flame is reached when the excess of primary air brings the mixture near to the limits of inflammability, or, precisely speaking, when the rate of inflammation of the mixture is reduced below the velocity of the ascending gas mixture adjacent to the walls of the tube. The flame then gets detached from the orifice, rises and disappears.

The various phases are shown diagrammatically in Fig. 1.

In Fig. 1 (*e*) the inner cone, which has retreated, is shown as being arrested at the orifice of the narrow tube through which the mixed gases are led into the wider one. The arrest is due to the fact that in the present example the velocity of efflux through the narrow tube exceeds in all cases the velocity of inflammation of the mixture. The apparatus used by Smithells (Chem. Soc. Trans. 1892, **61**, 204) known as the flame separator (Fig. 2), depends for its action on the principle just mentioned. It consists of two cylindrical tubes of different diameter, made preferably of fireproof glass, one of which slides within the other through an india-rubber collar. A guide attached to the inner tube keeps it coaxial with the outer tube. Mixtures of an inflammable gas and air can be admitted through the lower end of the narrow tube by attaching a T-piece, or more simply by attaching it to a Bunsen burner. A two-coned flame can be obtained, and if the proportion of the gases is suitably adjusted for a velocity of inflammation intermediate between the upward velocity of the mixture in the wide tube and that in the narrow one, the inner cone will descend in the wide tube and come to rest at the orifice of the narrower one. If the outer cone be now slid down, a two-coned flame rests on the orifice of the narrow tube. The practical value of the appliance depends on the fact that it permits separate chemical and physical examination of the inner and outer cones and of the interconal gases, and in this way it has been of assistance in the study of the progress of combustion in complex gases.

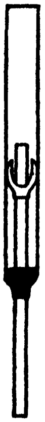

FIG. 2.

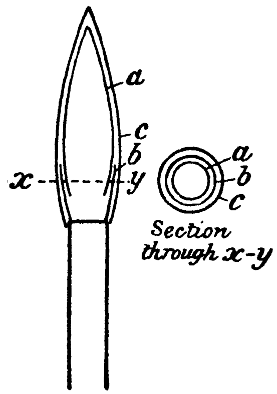

FIG. 3.

The influence of aeration on the structure of flames of carbon monoxide—air mixtures may be taken as typical and this mixture was chosen for the simplicity of the chemical reactions involved. Nearly all combustible gases met with in practice are either hydrocarbons or mixtures containing hydrocarbons such as coal gas. The greater complexity of the gases introduces additional features. The flames without " primary " air are rendered luminous by the separation of carbon in the shell of burning gas. Closer examination shows that this shell really consists of three distinct parts. The most conspicuous is the bright yellow luminous area (Fig. 3 (*a*)). The lower part of the flame is surrounded by a bright blue sheath or " calyx " (*b*). In addition the whole flame is encased in a dimly burning mantle (*c*). The interior of the shell contains the, as yet, unburnt gas. The relative brightness of some of these parts depend on the composition of the gas and the form of the orifice and conditions of burning. Luminosity varies with the composition of the hydrocarbons.

A high velocity of efflux reduces the luminosity of the flame. Examples of these influences may be seen in the form of non-aerated burners used for burning acetylene, and of batswing burners for coal gas. If the air ports of an ordinary Bunsen burner are gradually opened it is easy to follow the transition of the *calyx* into the inner cone and the luminous mantle into the outer cone which becomes non-luminous.

These two cones can be separated by means of the Smithells Separator and the interconal gases sampled and analysed. It will be noticed that the inner cone is furnished with a faintly luminous glow which has been termed the " aureole." The interconal gases themselves consist essentially of the four gases CO, H_2, CO_2 and H_2O diluted with the nitrogen from the air. No more than traces of hydrocarbons are present and in a separated Bunsen flame of coal gas no oxygen can be detected with ordinary methods of gas analysis. A typical analysis due to Smithells and Ingle (J.C.S. 1892, **61**, 209) of the interconal gases of a coal gas flame is: CO_2 4·2%, H_2O 16·0%, CO 8·8%, H_2 9·3% and N_2 62%.

The four actual products of combustion are the components of the " Water Gas Equilibrium System " and the value of the equilbrium constant $\frac{[CO][H_2O]}{[CO_2][H_2]}$ for the analysis given is 3·7 which corresponds to a temperature of about 1,500°C.

Haber and Richardt (Z. anorg. Chem. 1904, **38**, 5) showed that figures so calculated agreed with those obtained by measurements with thermo-electric couples. The inference is drawn that in the passage of the air–gas mixture through the inner cone of a Bunsen flame, the reaction is carried to thermal equilibrium at the temperature attained. The absence of oxygen is to be noted and this gives rise to the term " reducing flame " as applied to the inner part of a coal gas flame.

In industry the term " diffusion " flame (*v. supra*) is applied to a type which is a variant of one mentioned above. If the emerging stream of fuel gas is surrounded by a concentric stream of air under conditions such as to retard interdiffusion, the combustion can be delayed. The velocities and densities of gas and air should approximate, if necessary by preheating the air. By this means so-called " diffusion " flames of great length and radiating area can be produced, and their properties have been studied by S. P. Burke and T. E. Schumann (Ind. Eng. Chem. 1928, **20**, 998). Delayed aeration promotes liberation of incandescent particles over a large area. This is useful for the rapid and uniform heating of large furnaces. Such flames may be open, or formed in heat-resisting tubes which radiate upon the furnace charge. This device helps the control of furnace atmosphere.

Flame Temperatures.

The defining and measurement of the temperature of gases presents difficulties which do not arise when dealing with solids and liquids. If a thermometric instrument is immersed in a solid or liquid until equilibrium is reached then a tolerably precise indication of temperature can be obtained. When dealing with gases in general new features appear. Gases, according to the kinetic theory, consist of molecules in linear motion and therefore charged with kinetic energy of translation. This energy can be measured by the pressure exerted by a fixed quantity of gases on the walls of a confining vessel. This pressure is taken as a measure of the temperature of the gas, either by direct measurement or by some instrument calibrated against the pressure. Gases may be charged with energy in other forms, *e.g.* that associated with the quantised electronic, vibrational and rotational states of the constituent molecules. In a system in equilibrium, the total energy of the system will be distributed between these quantised states and the kinetic energy of the molecules according to the Maxwell-Boltzmann law. If the equilibrium is disturbed, an appreciable time may elapse before the energy is redistributed in the normal manner. This is especially true of flame gases which are or have been in a state of intense chemical activity, and where chemical and physical equilibrium may not be established. In these circumstances the temperature indicated by a particular measuring instrument will depend on whether or not it is affected by energy of a particular form. As an example, a thermocouple inserted in a stream of hydrogen containing free atoms would indicate a higher temperature than that corresponding to a translational energy of the component molecules and atoms, since the catalytic recombination of the atoms on the surface of the wire would result in the release of the chemical energy of reaction. Similarly in a system in equilibrium, which is emitting radiation, one may determine the temperature from a spectroscopic examination of the radiation, *e.g.* by the distribution of intensity in the vibrational and rotational structure of a band spectrum. When equilibrium is not attained, the temperature determined by this means may be different from that measured by the kinetic energy of the gas, but is none the less significant as the vibrational and rotational levels contribute to the total energy of the system.

The temperature of the sodium vapour in electric discharge lamps appears to exceed 2,000° judged by brightness and to be only one-tenth of this judged by direct measurement. Again the bright inner cone of the Bunsen flame judged from the intensity of its radiation is the hottest, whereas thermometric measurement shows it to be the coolest region of the flame. The inner cone is a region of intense chemical activity, the source of a visible radiation in excess of that emitted by the adjacent gases which, judged by their translational kinetic energy, are at least as hot.

For a fuller discussion of the meaning of gas temperatures, *see* J. G. Bennett and M. Pirani, J. Inst. Fuel, 1939, **12**, 1–45, Special Issue, March 12.

The term " flame temperature " is sometimes applied to a figure calculated on the assumption that the known heat of combustion of the combustible is distributed without loss among the theoretical products of combustion. These figures are always arbitrary because they depend on the nature and extent of the assumptions made—the specific heats of gases at high temperature, the degree of dissociation of the products into simpler molecular radicals or atoms. Such calculations have a certain use in making estimates of comparative thermal intensity and usefulness of fuels. The use of these calculated " theoretical flame temperatures " is, however, limited because they vary little for a wide range of fuels. The combustion of carbon with air to form CO_2 with its associated nitrogen gives about 900 calories per litre of gaseous products. The combustion of hydrogen with air to form steam with its associated nitrogen gives almost exactly the same quantity of heat (net) per litre of products. As most fuels consist of C and H in various atomic combinations, and having only small heats of formation, the composition of a fuel consisting essentially of carbon and hydrogen has no large influence on the " thermal intensity," or " flame temperature " in this sense, of the products. Actually the usefulness of the fuel in practice will, in most cases, depend on other considerations.

Most flames are composed of or bounded by thin films and their external surface encloses a quantity of unburned or partly burned gas. It is not customary to speak of the temperature of such a flame as meaning the average thermal state of the burning films and the included gas. The temperature attainable by the combustion of gas usually means the temperature which would be indicated by a thermometric instrument wholly immersed and in thermal equilibrium with its surroundings in a specified region of combustion. Such a temperature is obviously lower than the " theoretical flame temperature " mentioned above. Combustion is not instantaneous and energy is lost by radiation. It is difficult to make such measurements in thin films of flame; but is more practicable in " volume " flames, produced by burning ready-made mixtures of combustible gas and air.

An extensive and critical account of the measurement of flame temperatures has been given by G. Ribaud, Y. Laure and H. Gaudry (J. Inst. Fuel 1939, **12**, S. 18), and B. Lewis and von Elbe (*op. cit.*) have reviewed the optical methods.

The following is a summary of the methods used by different observers:—

(1) *Direct Measurements with Thermo-electric Couples.*—This method is limited by the melting-points of platinum and its alloys, which are below the temperatures attainable by combustion of hydrocarbons with air. Moreover, allowance must be made for the loss of heat by radiation from the glowing wires. This is done by making measurements with couples of different diameter and extrapolation to zero diameter. In some cases a suction pyrometer can be used effectively. The flame gases are drawn at high speed over the junction of the couple so that the junction can attain or approach equilibrium with the gases.

(2) *Direct Measurements with Resistance Thermometers.*—Resistance thermometers of very fine wires have been used for measuring the temperatures of flame produced in explosions. Resistance thermometers have also been used for measuring the temperatures of jet flames, provision being made for the loss of heat radiated from the glowing wire. These measurements are also limited to temperatures below the melting-point of platinum. The method used by E. Griffiths and J. H. Awbery at the National Physical Laboratory was of this type (Proc. Roy. Soc. 1929, A, **123**, 401).

(3) *Brightness of Suspended Particles or Vapours.*—The temperatures have been deduced from brightness of particles suspended in flames. Such measurements are based on the laws of radiation and are independent of the refractoriness of solids. They enable measurements to be carried into the more important range of temperatures attained when fuels are burned both with air and with oxygen.

This method was first applied by Kurlbaum to luminous flames where the radiating particles were free carbon. Féry extended this method to non-luminous flames by colouring them with salt vapours and his method has been widely applied. Féry observed the continuous spectrum emitted by a source, *e.g.* a carbon filament lamp when a flame coloured with salt vapour was interposed. When the brightness of the lamp was varied the D lines would either stand out more brightly or less brightly than adjacent parts of the spectrum. When the lines merged into the spectrum it was assumed that the temperature of the salt vapours equalled that of the source. The temperature of the source would be measured independently with an optical pyrometer. The radiation of the salt vapours is assumed to be purely thermal and their temperature equal to that of the flame gases. The assumptions underlying this method have been challenged, but the method has been very widely used and on it are based most of the measurements recorded in current literature.

(4) *Colour Brightness.*—A more recent development of flame thermometry is the use of colour brightness pyrometers. The ratio of the brightness of the red and green bands of the radiation from the flame is dependent on the temperature of a source. If the relationship is known it may be used to measure the temperature of luminous flame. Such measurements give higher results than those given by total brightness pyrometry.

(5) *Chemical Thermometer.*—Temperatures of flames have been inferred from the composition of the gases within the flame which Haber called the "chemical thermometer." It is assumed that the flame gases are in chemical equilibrium and that the relation of this to temperature is known. The hot gases are withdrawn from the flame by a water-cooled capillary whereby they are sampled cold for analysis without, it is assumed, change of composition. The results depend on a number of assumptions, partly as to experimental method and also as to thermochemical data. The validity of these assumptions is uncertain but, at least for temperatures below about 2,500°C., the results are in substantial agreement with those obtained by other methods.

(6) *Range of α Particles.*—When α particles are projected through a layer of gas the range of the particles depends on (*a*) the intrinsic stopping power of the gas and (*b*) its absolute temperature. By measuring the capacity of non-luminous gases of a coal gas/air flame to stop particles, Shirodkar (1933) calculated the temperature of the flame gases as 1,845°C.

FLAME TEMPERATURES.

The following results are taken mostly from a table given by Lewis and von Elbe (*op. cit.*). They have been measured by sodium-line reversal unless otherwise stated:

Mixture.	Per cent. combustible.	Flame temp. °C.
Hydrogen/air	31·6	2,045
,, /O_2	67	2,487
Atomic hydrogen	100	2,515, method 3 (Griffiths and Awbery *l.c.*).
Carbon monoxide/air	32	2,100
Carbon monoxide/O_2	60	2,905
Methane/air	10	1,875
Butane/air	3·2	1,895
Acetylene/air	9·0	2,325
Acetylene/O_2	33·0	3,007
Ethylene/air	7·0	1,975
Ammonia/air	21	1,700
Natural gas/air	9·0	1,930
Coal gas/air	17·6	1,918
Carburetted water gas/air	18·8	1,930
Coal gas/air	—	1,883, method 3 (Griffiths and Awbery).
Coal gas/air	—	1,886, method 2 (Griffiths and Awbery).
Coal gas/air	—	1,845, method 6

Radiation from Flames.

The radiation emitted by flames has been studied extensively with two principal objects, the elucidation of the mechanism of combustion and the utilisation of the radiant energy in increasing the efficiency of heating processes. Although the problem of the origin of the radiation has attracted much attention, it is still uncertain whether the process is thermal or chemiluminescent in character, or both, *i.e.* whether or not the energy states concerned in the emission are in thermal equilibrium with the remainder of the system according to the Maxwell-Boltzman distribution law. The conception of thermal equilibrium and the relation between the kinetic energy of the molecules and their electronic, vibrational and rotational energy is discussed in the preceding section on flame temperature. In general it is to be expected that in the flame front where chemical change is most active, particular species may be formed in an excited state, giving rise to emission which is characterised as chemiluminescent. In the outer regions of the flame the tendency will be for the establishment of thermal equilibrium consequent on the " degradation " of " ordered " energy of chemical reaction and the radiation emitted will be thermal in character.

Experiments carried out to test this point are not entirely conclusive. Schmidt (Ann. Physik. 1909, [iv], **29**, 1027) made measurements of the spectral brightness in the infra-red region of a coal gas flame in a Meker burner. These measurements were made a short distance above the cone, and were considered to establish the thermal nature of the infra-red radiation in this part of the flame. On the other hand, in " cool " flames, where visible light is emitted, the temperature as determined thermometrically is of the order of 300°C., and hence it would appear certain that the radiation is chemiluminescent. The whole question merits further study, with particular reference to modern conceptions of the significance of flame temperature discussed on p. 240.

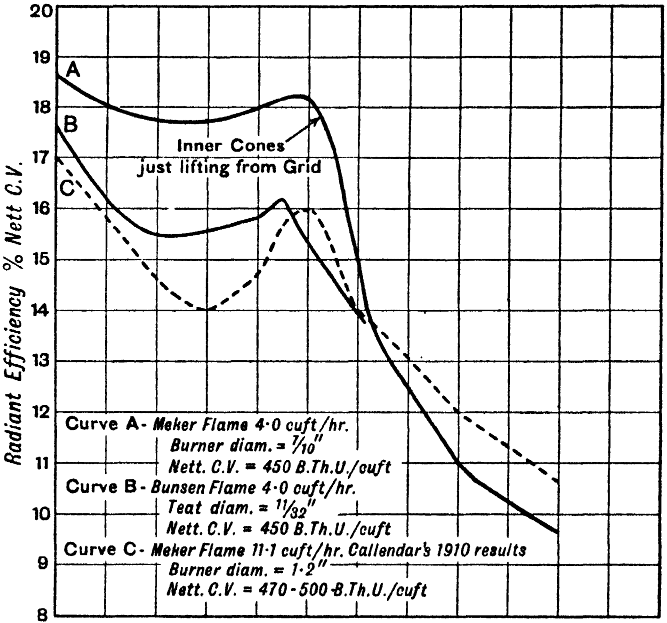

FIG. 4.

(Reproduced by permission of the Institution of Gas Engineers.)

The distribution of energy through the spectrum has been examined for many flames. An important fact is that the emission in the visible and ultra-violet regions represents only a very small part of the total energy emitted.

Almost all the radiant energy of the hydrogen flame is in the band at 2·8μ emitted by the water molecule. Similarly, with the dry carbon monoxide flame, most of the energy is associated with the band at 4·4μ characteristic of CO_2. When water vapour or hydrogen is present in this flame, the water band at 2·8μ appears, but the total radiation is greatly diminished. In the case of hydrocarbon flames, as might be expected, both the CO_2 and H_2O bands are observed in the " non-luminous " flames, while when the flames are " luminous," due to restriction of primary air, sensibly " black body " emission from the incandescent particles of carbon is observed, the position of the maximum emission being determined by the temperature of the flame according to the Wien displacement law.

The radiation from flame is important in practice because it supplements the transfer of heat by convection while being free from its limitations. It is particularly important in connection with the use of gaseous fuels and must be considered in relation to the structure and size of flames. In practice substantially all flames involve the same gaseous products as a hydrocarbon flame, and it is convenient therefore to take the Bunsen flame as typical.

The quantity of energy radiated by a flame of coal gas depends on the degree of aeration of the gas mixture supplied to the burner. Fig. 4 taken from a paper by H. Hartley (Inst. Gas. Eng. 1932–33, **82**, Comm. No. 63, 4) shows the results obtained by Callendar for a Meker burner (C) and by Hartley for a Meker burner (A) and a Bunsen burner (B). The minimum radiation, about 10% efficiency, is emitted by fully aerated flames. As the aeration is reduced the size of the flame and the radiation emitted increase to a peak with 16–18% when about half the air is supplied before combustion. Further reduction of primary air causes a slight fall in the emission, but the output of radiation increases as the aeration falls to zero and the flame acquires " luminosity " owing to the separation of carbon. The effect of this carbon from the coal-gas flames is less than might be expected.

R. T. Haslam and others (Ind. Eng. Chem. 1925, **17**, 272; 1927, **19**, 4) obtained results which can be harmonised with these figures. With acetylene, however, the radiation was 6·9% when the primary air supplied was 50% of theoretical. The emission rose to 28·2% from the luminous flame with no primary air, and is an extreme example of the influence of carbon particles in the flame. Acetylene, it must be remembered, is an endothermic compound.

Hartley (*l.c.*) has examined the distribution of the radiant emission through the various parts of an aerated coal-gas flame (C.V. 500 B.Th.U. per cu. ft.), in which the total radiation represented 13·5% of the calorific value of the gas burned. It was found that 85% of this energy was emitted by the outer cone and the surrounding heated products of combustion, while most of the remainder came from the inter-conal region.

The effect of increasing thickness of the flame on the intensity of the emitted radiation has been studied extensively, owing to its obvious importance in industrial applications. It can be shown that the total radiation $E=K(1-e^{-kx})$ where K and k are constants and x is the thickness of the flame. In practice it is found that even luminous flames containing free carbon particles are relatively transparent to their own radiation, so that E is directly proportional to x for small values of x, while it is not until x is of the order of 100 cm. in the case of a coal-gas flame that further increase produces no further increase in E (Callendar, J. Gas Lighting, 1910, **111**, 644).

A. Shack (Z. tech. Phys. 1924, **5**, 267, and " Industrial Heat Transfer," 1933, Chapman and Hall) has considered the effect of pressure, temperature and thickness on the radiation received from unit surface of a layer of carbon dioxide and water vapour, and has published curves from which the intensity of such radiation may be calculated under particular conditions. His values show good agreement with experiment.

The practical application of the radiation from flames in industrial heating processes has been the object of more attention recently. W. E. Garner's observation that the addition of hydrogen to a carbon monoxide flame decreases the total radiation provides an explanation for the furnaceman's preference for the " soaking " heat of producer gas as opposed to the " cutting " heat of water gas, whilst the value of the presence of tarry particles in producer gas is well established.

Experiments have been made on the addition of hydrocarbons to mixtures such as blast-furnace gas in order to increase the radiation. The application of large diffusion flames and luminous flames from rich hydrocarbon mixtures has been studied by Williams and Cone (J. Amer. Ceram. Soc. 1932, **15**, 501), Hepburn and Weller (Metal Progress Aug. 1935), Hottel and Broughton (Ind. Eng. Chem. (Anal.) 1932, **4**, 166) and others.

EMISSION IN THE VISIBLE AND ULTRA-VIOLET REGIONS.—The emission of band spectra in the visible and ultra-violet regions is the result of a change in the electronic energy state of the emitting molecule. In general, each transition from one electronic state to another gives rise to a system of bands, of which each individual member corresponds to a transition between particular vibrational states of the molecule. The individual lines of the band correspond to the transition between particular rotational energy states. The analysis of these spectra according to modern theory permits the determination of the molecule responsible for the emission in the case of diatomic and some simple polyatomic molecules. In addition spectroscopic data give information as to the absolute sizes, moments of inertia and heats of dissociation of the molecules, while dissociation constants and specific heats of gases may be evaluated under some conditions. The mechanism of the emission of continuous spectra in the visible and ultra-violet regions, apart from the emission of thermal radiation by solid bodies, is less well understood. In general, if a transition occurs to an electronic state having a potential energy function of the " repulsive " type, dissociation of the molecule follows, accompanied by the emission of continuous radiation.

The emission of the hydrogen flame in these regions is almost entirely confined to the bands of the OH radical in the near ultra-violet at 3,248, 3,122, 3,064, 2,875, 2,811 and 2,608 A. In addition there is a faint continuous emission of unknown origin. The flame of dry carbon monoxide shows a diffuse banded system superposed on a continuous spectrum extending through the visible and near ultra-violet, which has been shown by Fowler and Gaydon (Proc. Roy. Soc. 1933, A, **142**, 362) to be identical with that observed in the afterglow of carbon monoxide excited in a discharge tube. This spectrum is considered to be characteristic of the formation of excited carbon dioxide molecules by the direct interaction of carbon monoxide and oxygen. Weston (*ibid.* 1925, A, **109**, 176) has shown that as water vapour or hydrogen is added, the OH bands appear and increase in intensity, while the CO_2 bands and the continuous spectrum diminish. With most hydrocarbons bands of CH at 4,317, 3,888 and 3,140 A and of C_2, the Swan bands at 4,737, 5,165 and 5,635 A, etc., are emitted, together with the above mentioned systems. In addition there occurs a complex and extensive system of bands in the near ultra-violet and visible region first noted by Vaidya (*ibid.* 1934, A, **147**, 513) in the ethylene flame and hence known as the "ethylene flame" bands. The emitter of this system is uncertain; Vaidya considered it to be the radical CHO, but others have suggested CH_2 (Bell, *ibid.* 1937, A, **158**, 429) and $HCHO$ (Kondrateev, Acta phys.-chim. U.S.S.R. 1936, **4**, 556; Smith, Proc. Roy. Soc. 1940, A, **174**, 110). The continuous emission from incandescent carbon particles previously mentioned extends into the visible region to an extent depending on the flame temperature.

The relative intensities of these bands vary in a somewhat complex manner with the nature of the combustible, degree of aeration and the zone of the flame examined.

The spectra of certain special forms of flame, *e.g.* the "cool" flame, and of the less usual combustible substances, have also been the object of considerable investigation. It is beyond the scope of the present article to deal with all these cases, but the list of references given in the next column, indicating the nature of the flame and of the emission bands observed, while by no means exhaustive, should serve as a guide to the literature of the subject.

The conclusions which have been drawn from these observations are in many cases of doubtful value, as insufficient consideration has been given to the complexity of the mechanism of the emission of spectra in flames, and to the difficulty of interpreting the chemical processes from spectroscopic data. This matter is discussed by E. C. W. Smith (Proc. Roy. Soc. 1940, A, **174**, 110). In spite of these limitations the observation of the spectrum is almost the unique source of information as to the part played by free radicals and similar reactive species in combustion processes. In general it would seem that the spectra indicate some degree of disruption of the combustible molecule followed by rearrangement to stable and semi-stable molecules, which is not in accord with most current theories of combustion. On the other hand, so little is known of the nature of the kinetic processes involved, that it is doubtful whether any of the theories, "hydroxylation," "peroxidation," "chain theory" do more than give a representation of the mechanism which is more or less useful for particular purposes. So little is known of the mode of transfer of the energy of chemical reaction that to attempt to prove that any particular theory represents the actual course of the molecular and atomic encounters is quite useless. In particular, little is known of the part played by radiation in the transfer of energy from reacting to unreacted molecules, and it would probably be possible to account for all known data on the assumption that this energy is radiated in the far ultra-violet and absorbed by the surrounding molecules.

Reference.	Flame.	Bands observed.
Bell (Proc. Roy. Soc. 1937, A, **158**, 429).	CH_4 $CH_3{\cdot}OH$ $CH_3{\cdot}CHO$	C_2, CH, OH, CO_2, "Et flame."
	$H{\cdot}CHO$	CO_2, OH.
Emeléus (J.C.S. 1926, 2948).	$(C_2H_5)_2O$: Cool flame	Fluorescent bands of $H{\cdot}CHO$.
	Normal flame	C_2, CH, OH, "Et flame."
Fowler and Badami (Proc. Roy. Soc. 1931, A, **133**, 327).	H_2 in N_2O	NH, OH, NO, NH_2(?)
Fowler and Gregory (Phil. Trans. 1919, A, **218**, 351).	NH_3	NH, NH_2 (?) NO.
Fowler and Vaidya (Proc. Roy. Soc. 1931, A, **132**, 310).	CS_2	S_2, CO, SO_2, CS.
	H_2S	S_2, SO, SO_2, OH.
Kitagawa (Proc. Imp. Acad. Tokyo, 1935, **11**, 262).	Br_2 in H_2.	Br_2.
Rassweiler and Withrow (Ind. Eng. Chem. 1932, **24**, 528).	Flame in cylinder head of petrol engine.	C_2, CH, OH, "Et flame."
Vaidya (Proc. Indian Acad. Sci. 1935, **2**, A, 352).	Benzene Toluene Phenol Resorcinol Pyrogallol Benzaldehyde Benzoic acid Diphenyl oxide	C_2, CH, OH, "Et flame."
	Aniline Nitrobenzene Pyridine	C_2, CH, OH, "Et flame," CN, NO.

Products of Combustion.[1]

When a fuel such as town gas burns in a flame with free access of air, combustion to CO_2 and H_2O is remarkably complete. These major products of combustion are harmless, although in certain water-heating installations provision must be made for the disposal of condensed water, amounting as it does to approximately 1 gallon per 100,000 B.Th.U. generated.

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[1] The chemistry of combustion and details of its probable mechanism are discussed in the article EXPLOSIONS, GASEOUS, Vol. IV, pp. 417 *et seq.*

The products of combustion contain in addition minor constituents such as **CO**, oxides of sulphur, and oxides of nitrogen which have important influences upon the domestic and industrial application of flames. In the case of imperfect combustion of gas a characteristic unpleasant odour is often observed. The precise nature of the compounds causing the odour has not been determined, although formaldehyde has been identified. The presence of acetylene has also been claimed.

Because of its poisonous character, the conditions causing formation of **CO** and the extent of its production have received much attention, and standards have been laid down as to what constitutes good practice. The amount of **CO** in the products of combustion of flames burning freely in the open, whether of the luminous or Bunsen types is extraordinarily low. On the other hand, the proportion of **CO** may rise when attempts are made to apply such flames. The conditions which favour incomplete combustion and therefore an increase in the **CO** in the products are: (1) inadequate access of air to the flame; (2) contamination of the air supply with products of combustion; (3) chilling of the flame; and (4) in the case of Bunsen flames, breaking of the inner cones. The imperfect supply of air and removal of products of combustion may be general or local, as a result of distortion of the flame by a massive solid body, and the **CO**-production will be increased if the interfering body is cold. For these reasons the **CO**-output of an appliance usually increases rapidly when it is worked above a specified rate, and although perfectly satisfactory at the rate for which it was designed, may become dangerous if overloaded.

Completeness of combustion is usually judged by the CO/CO_2 ratio in the products of combustion, the small amount of **CO** being determined by I_2O_5 oxidation. For domestic appliances the CO/CO_2 ratio should not exceed 0·02 at 100% pressure overload. (British Standard No. 717—1936.)

The following figures for free-burning flames show how complete combustion may be:

	Parts of CO per 10,000 of gas burned.
Flat-flame and Argand Burners .	1
Bunsen Burner, Meker Type .	1
Bunsen Burner, well-aerated .	1
Bunsen Burner, air-shutter closed to give luminous flame . .	2

Since 1 cu. ft. of town gas produces about 0·5 cu. ft. of CO_2 and 4–4·5 cu. ft. of air-free products of combustion, it will be seen that the actual concentration of **CO** in flue gases may be very low, even without the dilution with excess air which invariably occurs.

For comparison it may be noted that town air contains about 5 parts of **CO** per million, rising to 20 parts in foggy weather, and that 80 parts per million has been recorded in streets with much motor traffic. Detailed studies of methods of determining **CO** and the **CO**-production of a variety of gas appliances have been made by Hartley and Davies (J.S.C.I. 1927, **46**, 201T), by Masterman and co-workers (Trans. Inst. Gas. Eng. 1931–32, **81**, 142–189; 1935–36, **85**, 95–166), and by J. W. Wood and G. B. Howarth for the Gas Investigation Committee of the Institution of Gas Engineers (15th, 17th, 19th, 21st and 25th Reports, *ibid.* 1924–25, 1925–26, 1926–27, 1927–28, 1929–30).

Oxides of nitrogen in small quantity are found in the products of combustion of practically all fuels, probably due to reaction between the oxygen and nitrogen of the air at the high temperatures involved. In the case of town gas a further possible source is the combustion of traces of ammonia and cyanogen compounds remaining in the gas. The presence of **NO** in gas retort settings and the exit gases from power plants to the extent of 0·05 grains per cu. ft. has been established. The oxides of nitrogen exist chiefly as **NO** in the zone of combustion, but this is slowly converted to NO_2 and in the presence of water may play an important part in corrosion phenomena (*see below*). The concentration of NO_2 rarely attains a sufficiently high value to have troublesome physiological effects, but damage to artificial silk goods dyed with certain dyes has been traced to oxides of nitrogen in the atmosphere. Oxides of nitrogen probably play a part also in the deterioration of leather goods, book-bindings and photographic goods, although this was formerly attributed almost wholly to sulphur compounds. The **NO**-production in the case of town gas amounts to about 1 part of **NO** per 10,000 volumes of gas burned (Inst. Gas Eng. Trans. 1931–32, **81**, Comm. No. 36, 66).

Nearly all the sulphur of solid fuels and all the sulphur of liquid and gaseous fuels burns to oxides of sulphur in the course of combustion, by far the greater part in the gaseous phase being in the form of SO_2. Conversion to SO_3 is relatively slow, and commercial methods for the removal of the oxides of sulphur from waste gases usually depend upon fixing them as sulphites and subsequent oxidation to sulphates.

At the present time a typical value for the sulphur content of a town gas is 22 grains of sulphur per 100 cu. ft. This gives rise to 0·01% by volume of SO_2 and SO_3 in the theoretical air-free products of combustion. These oxides are objectionable in a number of ways: (1) their pungent odour, especially that of SO_3, restricts the development of flueless appliances; (2) they lead to corrosion and eventual destruction of gas appliances; (3) in the industrial field the sulphur compounds may have an adverse effect upon non-ferrous materials, and appreciably increase the scaling losses when working steel; glass may acquire a " bloom " during working.

These objections have led to a demand for sulphur removal and some gas companies are sending out gas with only 10 grains of sulphur per 100 cu. ft. It is probable that new methods of gas production and purification will result in even lower sulphur figures. This is the more likely since recent work has shown that while *any* sulphur removal would be beneficial, reduction in corrosion troubles is not proportional to the reduction in the sulphur content of the gas, and that reduction to below 5 grains per 100 cu. ft. is desirable.

The commoner materials used in the construction of gas appliances may be placed in descending order of their resistance to corrosion by products of combustion under conditions where the water vapour simultaneously formed is almost completely condensed, as follows: tin, solder, lead, aluminium, copper, brass, zinc and iron. In the case of zinc the sulphur acids are almost quantitatively taken up. Lead is peculiar in showing increased corrosion at low sulphur concentrations. This is presumably due to the action of the small amounts of nitric acid formed by the oxidation of the NO produced during combustion, and failure to form a protective coating of lead sulphate.

Tests have also been made with the same materials under conditions of partial condensation and re-evaporation. The materials remain in substantially the same order, but corrosion is aggravated by local attack and the formation of localised deposits, some of them voluminous, such as would choke flue-ways and interfere with combustion. As might be expected, the deposits consist largely of basic sulphates of the metals named. Apart from the question of sulphur it has been shown that great importance attaches to the composition of the furnace atmosphere in the heat treatment of metals, and that bright finished work cannot be economically produced in a " reducing " atmosphere resulting from the indiscriminate admission of excess gas to the furnace.

References.—Wood and Parrish, " Corrosion by Products of Combustion," I (Trans. Inst. Gas Eng. 1933–34, **83**, Comm. 76, 73); II, Wood and Parrish (*ibid.* 1934–35, **84**, Comm. 100, 246); III, Wood and Eastwood (*ibid.* 1935–36, **85**, Comm. 121, 167); IV, Wood and Eastwood (*ibid.* 1936–37, **86**, Comm. 140, 58); Wood and Taylor (*ibid.* 1939, Comm. 224); Millett and Cobb, " Scaling of Mild Steel in S-free and S-Containing Furnace Atmosphere " (*ibid.* 1935–36, **85**, Comm. 127, 609); Fells, " Use of Town Gas in the Steel Industry " (*ibid.* 1933–34, **83**, Comm. 87, 598).

Combustion Characteristics.

As fuels are used to generate *heat*, the principal property of a fuel gas is therefore its calorific value, or the number of B.Th.U. developed per cu. ft. of gas burned. It does not follow that the gases with the highest C.Vs. are the most suitable for a public supply, in fact, constancy of C.V. is in practice more important than the precise value adopted.

Under the Gas Regulation Act, 1920, the initial selection of the calorific value of the gas to be supplied in any area in Great Britain was at the discretion of the local gas authority, without restriction as to composition so long as the " declared calorific value " is maintained. By far the greater part of the gas now supplied has a C.V. between 470 and 500 B.Th.U. per cu. ft., and there is a tendency to reduce the variety of declared calorific values in use.

It is found, however, that constancy of C.V. does not necessarily ensure uniformity of performance in gas appliances. The manner of combustion of the gas varies and these differences are loosely referred to as the " combustion characteristics " of the gases. For some time the technicians of the gas industry have been seeking methods of defining and measuring " combustion characteristics " and expressing the property numerically. Wood and Eastwood have prepared a critical review of the literature of the subject, with an extensive bibliography, for the Joint Research Committee of the Institution of Gas Engineers and Leeds University (Trans. Inst. Gas. Eng. 1937–38, **86**, Comm. 166).

Chemical composition fails as a criterion of combustion characteristics, as there is no simple and recognisable relationship between composition and behaviour on combustion; further, changes in composition, *e.g.* in the heavy hydrocarbons, not detectable with certainty by ordinary methods of analysis, may cause significant differences in the manner of combustion. Small quantities of accelerators or retarders, too small to measure directly, may also be present. The " C Function " put forward by the American Gas Association is a criterion or combustion characteristic which can be calculated from the chemical composition of the gas (*ibid.*).

Density or specific gravity is a most important physical property of a fuel gas, since variations in density affect both thermal delivery and the degree of primary aeration of atmospheric burners. Close regulation of both these properties (C.V. and density), however, does not of itself guarantee uniformity of performance in gas appliances. For this reason the Wobbe Index, *i.e.* $\left[\frac{\text{Calorific Value}}{\sqrt{\text{Sp.Gr.}}}\right]$, popular on the Continent, is only of limited service as a combustion characteristic (*see* review by Wood and Eastwood, *l.c.* p. 60).

The behaviour of a gas burner is closely related to the flame-speed curve of the gas (*q.v.*), but this curve does not give a single numerical value characteristic of the gas. The maximum flame speed is unsuitable for characterising the gas since atmospheric burners do not normally work at air-gas ratios corresponding with the maximum flame speed of the gas used, but at a lower value where flame speed is very sensitive to changes in air-gas ratio. An interesting and useful derivative of the flame-speed curve, Minchin's " D Function," is described in the review mentioned, p. 65.

In view of the defects of the criteria of combustion outlined above, the idea of observing the behaviour of gases in carefully standardised Bunsen burners has led to several attempts in this direction. The results are composite and empirical, and reproducibility depends upon the production of the test burners to very exact dimensions and their use under carefully standardised conditions.

Thus, Ott (Wood and Eastwood, *l.c.* p. 44) opened the graduated air-shutter of his burner until the flame was either unsteady (FZ—Flackerzahl) or actually struck back (RZ—Rückschlagzahl) and the corresponding reading was recorded as the " Ott Number " of the gas and is extensively used on the Continent. Hawes has devised an instrument giving a continuous record of the Ott Number of a gas (*ibid.* p. 49).

In the Hofsäss burner the air-shutter was fixed and variation in the height of the inner cone was taken as a measure of the gas quality. An alternative method adopted by Czako and Schaack (Wood and Eastwood, *l.c.* p. 52) was to determine the air-shutter opening necessary to reproduce a standard height of inner cone. A test burner known as the Aeration Test Burner (A.T.B.) working on these principles was also developed by the research staff of the Gas Light and Coke Company, London. It was critically examined by them and by Wood and Eastwood on behalf of the Institution of Gas Engineers (*ibid.*, Comm. 166,55; Comm. 189,72; Comm. 217). Two models " A " and " B " were produced, the latter being a most carefully constructed Bunsen burner with micrometer-controlled air-shutter. The quality of the gas is expressed on an empirical scale of " A.T.B. Numbers " corresponding with the opening of the air-shutter required to reproduce a standard cone-height.

The indications of the burner are not affected to any significant extent by ordinary variations in atmospheric temperature and pressure, but a change in the humidity of the air from a water-content of 1 to 2% by volume causes an increase of 3 A.T.B. units for a gas with an A.T.B. Number of 80. The effect of contamination of the atmosphere around the burner by products of combustion is even more marked, and the CO_2-content of the air near the burner should not exceed 0·2%. The lengthening of the inner cone of a test burner has even been applied to the detection and rough estimation of the degree of atmospheric pollution. A.T.B. Numbers (and some Ott and Czako and Schaack Numbers) of typical town-gas mixtures are indicated in the Inst. Gas. Eng. Communication mentioned, by Stewart (*ibid.*, Comm. 155,48) and by Haffner (*ibid.*, Comm. 202).

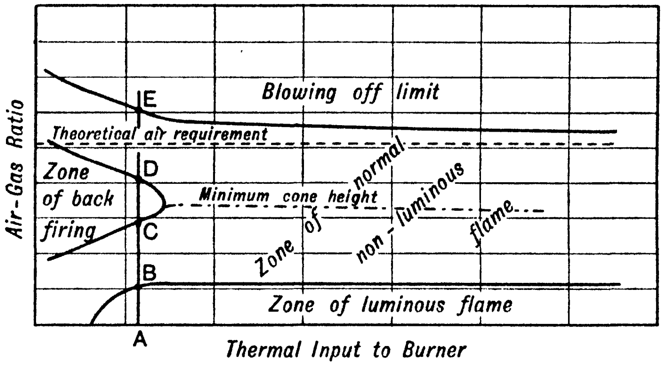


Fig. 5.

(*Reproduced by permission of the Institution of Gas Engineers.*)

It should be made clear that the object of test burners is to find the permissible limits of variation in gas quality for different types of gas-consuming appliances (lighting burners, cookers, gas-fires, etc.) and so to control the composition of the gas leaving the gasworks that troubles due to noisy operation, lighting-back, imperfect combustion, and blow-off may be avoided. For a typical town gas of C.V. 500 B.Th.U. per cu. ft. and an A.T.B. Number of approximately 75, a variation of ±15 A.T.B. units would appear to be tolerated in many appliances.

A graphical method of presenting combustion characteristics devised at the American Bureau of Standards (Tech. Paper No. 193, 1921) has been revived and developed by Fuidge, Murch and Pleasance (Inst. Gas. Eng. Comm. 223). It displays very clearly the properties of the principal fuel gases and commercial mixtures of them, and emphasises the almost inseparable parts played by the gas and burner respectively in effectively burning gas. The treatment is as follows: a standard burner is worked at a constant thermal input, and the behaviour of the flame and inner-cone are observed as the air-gas ratio is increased by mechanical means. One thus travels along a line such as AE on Fig. 5. At B the flame loses its luminosity, the inner cone then shortens and becomes more marked, until back-fire takes place at C. With increasing air-gas ratio, however, the flame-speed becomes lower and it is possible to relight the gas at point D and continue until the flame blows off at E. When a certain thermal input is exceeded as one moves towards the right of the diagram one no longer enters the back-fire area in passing from luminosity to blow-off.

The usable combination of gas-rate and air-gas ratio giving stable aerated flames on the standard burner is therefore that represented by the area on the combustion diagram lying between the heavy lines representing the limits of luminosity and blow-off, but excluding the area marked as the zone of back-fire.

Upon this combustion diagram an aeration diagram must be superimposed as shown by the light and dotted lines in Fig 6. These lines show the air-gas ratios which can be achieved when the standard burner is *injecting* air in the normal fashion with various combinations of gas pressure and size of orifice or jet for the gas. The composite diagram thus enables one to ascertain how much of the combustion diagram could be covered by the standard burner working in the normal fashion for given conditions of gas supply. The three principal constituents of town gas, hydrogen, carbon monoxide and methane show a remarkable diversity in the shape and extent of the boundaries of their combustion and aeration diagrams, and on this basis the paper referred to indicates the reasons for the suitability and unsuitability of numerous mixtures proposed for town gas supplies.

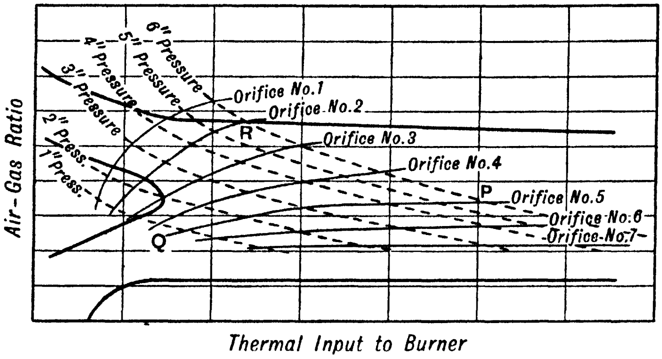


Fig. 6.

(Reproduced by permission of the Institution of Gas Engineers.)

Flame Speeds.—In burners of the Bunsen type the stream of gas issuing from the jet causes air to be drawn into the burner, and it is the character of the resulting air-gas mixture, particularly as regards rate of flame propagation, which determines the behaviour of the burner.

Results are generally presented in the form of curves showing the relation between the rate of flame propagation and the composition of the mixture. A series of curves for the principal fuel gases is given in Fig. 7. It will be noted that:

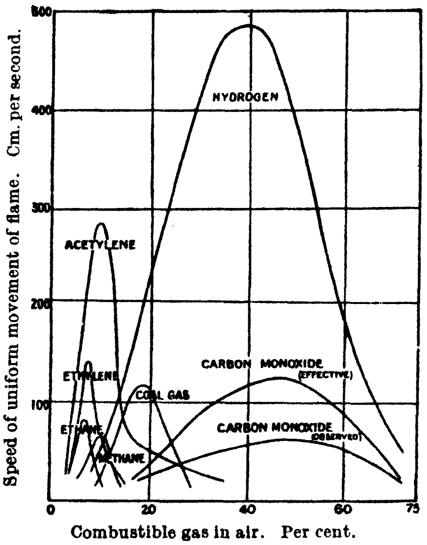


Fig. 7.

(1) Each curve exhibits a pronounced maximum.

(2) There is a remarkable difference in the maximum rate of flame propagation for individual gases, that for hydrogen being approximately seven times that for methane.

(3) For all curves the maximum rate of flame propagation is not attained when the air and gas are in the proportions theoretically necessary for complete combustion, but when there is an excess of combustible gas.

(4) The limits of composition of the air-gas mixture within which flame propagation will take place are very different for the individual gases (*see* "Limits of Inflammability," p. 237).

(5) The curves do not reach the base line but indicate a finite rate of flame propagation for mixtures at the limits of inflammability.

The curves shown in Fig. 7 were obtained by the "Static" method, *i.e.* by observing the rate of flame travel in a homogeneous stationary mixture confined in a horizontal glass tube 2·5 cm. diameter. There is an alternative "Dynamic" method of determining flame speeds due to Gouy which is perhaps of greater importance to burner designers, depending upon the measurement of the dimensions of the inner cone of a Bunsen flame fed with a homogeneous mixture of gas and air of known composition. The flame speed is given by:

$$V = \frac{Q}{\pi r\sqrt{r^2+h^2}}$$

where V = flame speed in cm. per sec.
Q = rate of mixture flow (air+gas) c.c. per sec.
r = radius of burner mouth (internal) cm.
h = height of inner cone in cm.

As the " cone " is not a true geometric cone, attempts have been made to obtain a more accurate estimate of the area of the actual envelope of the inner cone by using photographic enlargements of its image. Smith and Pickering have also measured the angle of the cone at a point 0·707*r* from the axis of the burner, this being the point at which for streamline-flow the speed of the mixture is equal to the mean speed which can be obtained from Q and πr_2, the area of cross-section of the burner. It may be here noted that the tip of the cone is always rounded, that the flame does not come right down on to the mouth of the burner, and that the base is generally slightly flared and overhangs the burner. These facts create some uncertainty in deciding upon the values of *r* and *h* which should be used for the calculation of V.

The speeds obtained by the static and dynamic methods (sometimes referred to as " tube speeds " and " burner speeds " respectively) however, differ from one another to a much larger extent than the experimental error revealed by comparing the results obtained by different workers using either of these methods, the " tube speeds " being approximately twice the " burner speeds." The work of Coward and Hartwell (J.C.S. 1932, 2676–84) and of Roeder (Nat. Adv. Comm. Aeronaut. (U.S.A.), Rpt. 1935, 532) has done much to explain the discrepancy by distinguishing between " fundamental " and " apparent " flame speeds. The burner speeds would appear to be the more suitable for use in calculations concerning the design of burners.

It is clear that given the flame-speed of a mixture, the process can be reversed and the size of inner cone can be calculated for a burner of specified dimensions. In practice there are several limitations not evident from the formula: (1) if the velocity of the air-gas mixture is sufficiently high to produce turbulent motion it behaves as though its effective flame-speed were higher than the true value—up to twice the value normally obtained. (2) According to the formula the cone could shrink to a flat disc across the mouth of the burner when $h = 0$. Actually back-fire occurs if the cone height shrinks much below 1·4 diameters, although this quantity depends upon the dimensions of the burner and properties of the gas being used. (3) The formula indicates no upper limit to the height of the cone, but above a certain height the cone lifts away or " blows off." The phenomenon is chiefly observable with slow-burning mixtures and is less well defined than back-fire. (4) In ordinary burners, preheating of the mixture on its way to the burner head produces changes in velocity which are difficult to allow for exactly.

It is important to note that no really satisfactory method has been devised for calculating the flame speed of a complex mixture like town gas from the flame-speed curves of its constituents, and actual determination is therefore essential in specific cases. Discussions of the dynamic method of determining flame speeds and of attempts to calculate flame speeds are given in Appendixes 1 and 2 to Trans. Inst. Gas. Eng. 1937–38, **86**, Comm. 166.

Flame-speed curves for binary and ternary mixtures of H_2, CO and CH_4, the principal constituents of town gas, have been given by Bunte and Litterscheidt (Trans. Inst. Gas. Eng. 1937–38, **86**, 19–21). The addition of " inerts," *i.e.* CO_2 and N_2 to a combustible gas lowers the flame speed of the mixture, CO_2 being more effective than N_2 approximately in proportion to its higher specific heat.

The effect of pressure upon rate of flame propagation is fully treated in EXPLOSIONS, GASEOUS (Vol. IV, 426).

The effect upon flame speed of preheating the mixture has been investigated by Passauer (Gas-u. Wasserfach, 1930, **73**, 313–19, 343–51, 369–72, 392–97). It causes an increase in the rate of flame propagation and also a slight displacement of the maximum towards the gas-rich side of the flame-speed diagram. If calculation is based upon the volume of gas and air measured at ordinary temperatures the apparent linear flame-speed is approximately proportional to the temperature of preheat measured on the absolute scale. The gravimetric rate of reaction is also proportional to the absolute temperature of preheat.

AERATION OF BURNERS.—The section upon flame speed indicates the great importance of the composition of the air-gas mixture in the case of atmospheric or Bunsen burners. The amount of air entrained is governed by many factors, including the gas pressure, specific gravity of gas, type of gas jet, size of air-shutter, resistances to flow encountered at the burner intake, in the burner body, and at burner outlet, and velocity to be imparted to the air-gas mixture in order to maintain stable flames at the burner outlet.

Air-injection has been examined by Pfotenhauer, J. S. G. Thomas and E. V. Evans, the American Bureau of Standards, and by Wood and Howarth (*see* Bibliography, Trans. Inst. Gas. Eng. 1937–38, **86**, Comm. 166 already quoted), but up to the present time only a few empirical and approximate relationships have been established.

Thus, for a given burner and gas injector working at a given pressure the quantity of air injected per hour is approximately constant. Since the gas delivery is inversely proportional to the square root of its specific gravity, the air-gas ratio is approximately proportional to the square root of the specific gravity. Increasing the pressure produces a fairly rapid increase in air-gas ratio in the initial stages, but when a certain figure is exceeded (which may lie between 1 in. and 3 in. water-gauge for low-pressure burners) the further increase in air-gas ratio is slight and it may even fall. On the other hand, delivery of the same quantity of gas through a smaller gas jet at higher pressure will lead to higher degrees of primary aeration.

The American Bureau of Standards assumes that there is a constant ratio between the momentum of the injecting gas stream and that of the air-gas mixture produced. Empirical measurements with one gas, together with the dimensions of the burner, allow a constant, R, to be determined which can be used for calculating the aeration of the burner under any other conditions.

The formula used is:

$$R = \frac{1{,}658{\cdot}5 \times \sqrt{H \cdot d}}{Q(r+d)(r+1)}$$

where R = momentum ratio constant.
X = cross-section of burner pipe in sq. ins.
H = gas pressure, ins. water gauge.
d = sp. gr. of gas (air = 1).
Q = gas rate in cu. ft. per hour.
r = primary air-gas ratio.

In normal British practice with low-pressure burners a primary air-gas ratio of 2 to 2·5 is used, or somewhat less than half the theoretical air-requirement of the gas. With slow-burning gases such as natural gas a lower outlet velocity is required and air-gas ratios of 4:1 and 5:1 are easily achieved.

It should be observed that in most cases the air-gas ratio of a burner falls as the burner becomes hot, reductions of 25% being common.

Types of Flames and Burners.—The non-aerated or luminous type of flame is now rarely used for the sake of the light it emits, but the original rat-tail and flat-flame burners still find extensive application. The gas is caused to expose a large area in both cases, and the whole of the air required for combustion is supplied by diffusion as secondary air. It must be emphasised that luminous flames of the type mentioned develop precisely the same amount of heat per unit of gas burned as do those of the Bunsen type. They cannot, however, be used where flame-contact is likely to occur owing to deposition of soot. On the other hand, they can be turned very low without extinction or back-fire and thus possess considerable advantages over the aerated type of flame where thermostatic control of heating is employed, as in automatic water-heaters. Quite recently the luminous flame has been re-adapted to use in gas fires.

Diffusion flames have already been referred to and find application almost exclusively in furnace practice.

In surface combustion appliances a mixture of gas and air in practically theoretical proportions is produced mechanically—usually with the aid of a small fan for the air-supply—and is forced through a porous refractory diaphragm. The surface of the refractory material attains a bright red heat and such devices have found widespread uses. Combustion is substantially complete when the air is some 5% in excess of that theoretically necessary for combustion, but the rate at which the combustible mixture can be supplied is subject to certain limitations. If fed too quickly the mixture burns on the exit face of the refractory slab which remains cold; and if fed too slowly the slab gradually becomes red-hot throughout and ignites the explosive mixture on the inlet side. According to measurements by Wood and Howarth using surface combustion grillers and water-heaters, the permissible rate of heat development was of the order of 36,000 B.Th.U. per sq. ft. of combustor surface per hour for a town gas of 470 B.Th.U. per cu. ft. Surface combustion has been claimed to accelerate combustion in certain types of furnace where the air-gas mixture does not pass through a diaphragm but is caused to impinge violently upon a rough bed of refractory material.

The forms taken by the aerated or Bunsen type of burner are too numerous to mention, their shapes and sizes being dictated by the purpose for which they are intended. To deal with gases of different qualities they are usually provided with adjustable gas nipples and air-shutters, although if gas quality is standardised and governors provided these means of adjustment may be dispensed with.

As has been pointed out already the ordinary aerated burner takes in only about half the air necessary for the combustion of the gas as primary air, and attempts are continually being made to increase the air-gas ratio with a view to securing more compact and hotter flames. The principal means adopted are to use better finished and accurately-centred injectors, carefully shaped air-intakes and Venturi tubes for the burners, and the insistence upon a better degree of finish for the internal passages of the burners so that resistances to the flow of the air-gas mixture shall be reduced to a minimum. The laboratory Meker burner is an example of an improved low-pressure burner in which these principles are applied, the air-gas mixture making its exit through a deep metal grid in the head of the burner and the individual flames coalescing to form a compact, solid and very hot flame. The air-gas ratio is higher than that in the ordinary Bunsen burner, reaching 60% of the theoretical air-requirement of the gas, according to Wood and Howarth.

In order to secure a higher flame temperature resort is sometimes had to preheating the air-gas mixture on its way to the burner head. Examples of this will be found in street-lighting burners and many industrial burners. If it is necessary to reach higher temperatures than are realisable in low-pressure burners, higher air-gas ratios can be achieved by the use of specially designed high-pressure gas burners, in which either the gas pressure is increased to about 72 in. water gauge, or air is supplied under pressure. The theoretical air-gas mixture may also be produced entirely by mechanical pre-mixture as in the Selas system.

The temperature reached in the flame may also be increased by the use of oxygen or air enriched with oxygen, the limiting case being the well-known oxy-acetylene cutting and welding burners, where the endothermic character of the acetylene augments the effect still further (*v.* Vol. I, 112).

Aerated flames have also been used in "submerged" burners for water-heating purposes, the direct contact between the water and the flames giving higher thermal efficiencies than when the heat has to be transmitted through the wall of a container as in normal practice.

In considering modern developments in the application of flames attention should be called to the exactness and ease with which heat can be supplied and controlled, and the cleanliness and compactness of the equipment. There is also a tendency to render the burners self-acting by the provision of automatic thermostatic control and of such conveniences as clock-controlled, catalytic, or electrical ignition.

H. J. H., E. C. W. S. and J. W. W.

"FLAMMIYORE" (*v.* Vol. IV, 556*a*).

FLASH LIGHTS.—A term usually applied to combustible mixtures which burn with a brilliant light and a flash of greater or less rapidity, and which are employed specially for photographic purposes. Slower-burning mixtures, which also yield a bright light on combustion, such as are used for signalling purposes, are known as flares (*see* BENGAL LIGHTS or INDIAN FIRE).

For photographic purposes, it is essential that the flash light should be (1) sufficiently brilliant, (2) of the desired rapidity, and (3) specially rich in actinic light. Of all the known available materials which, on combustion, yield a bright and highly actinic light, the metal magnesium stands pre-eminent; and the earliest and simplest methods of employing this substance consisted in projecting a definite quantity of the finely powdered metal into the flame of a spirit lamp.

Various contrivances have been devised for this purpose; one simple plan is to place the charge of magnesium powder in the bowl of a clay tobacco pipe to the mouthpiece of which is attached a rubber ball. A wick of cotton-wool or tow fastened round the outside of the bowl is wetted with methylated spirit; the spirit is ignited and on the ball being suddenly squeezed, the magnesium is thrown into the flame.

The next development consists in mixing the powdered magnesium with some highly oxygenated salt, such as potassium chlorate, in such proportion that the mixture, when placed in a small heap upon a metal tray, could be ignited by a match or taper, and would burn with much the same rapidity as a similar small heap of gunpowder. The proportion of equal parts by weight of potassium chlorate and magnesium has been found to give the best results.

A device much used for firing flash lights consists of a shallow trough fitted with a wooden handle and having at one end a trigger and hammer by means of which an "amorce" similar to those used in toy pistols, can be exploded to ignite the composition. The danger inherent in such mixtures was found to be greatly reduced by substituting barium chlorate for the potassium salt; and since potassium perchlorate has become a common commercial article, it is now usually employed in preference to the chlorates.

Mixtures of magnesium with certain nitrates of the rare earths have been made the subject of patents. One such consists of:

Magnesium powder . . .	10 parts
Thorium nitrate	10 „

and a rather less quick mixture contains:

Magnesium powder . . .	10 parts
Zirconium nitrate . . .	5 „

The addition of a small proportion of metallic cadmium has been suggested as giving increased actinic value, but it is questionable whether the improvement is justified by the expense.

One of the chief drawbacks to magnesium flash powders is the volume of white smoke of magnesium oxide which is produced on their combustion, and many efforts have been made to obviate this nuisance. Some of these are purely mechanical contrivances for withdrawing the smoke, but others are attempts to produce mixtures which shall emit little or no smoke. The two following mixtures claim to yield smokeless magnesium flash powders:

(1) Powdered magnesium, barium peroxide, with collodion. The charge of powder is blown by means of a pneumatic pump into a small iron crucible heated by a Bunsen burner.

(2) One part of magnesium powder mixed with 1 part of either silica ("infusorial earth"), barium sulphate, anhydrous calcium sulphate, kieserite (magnesium sulphate, $MgSO_4,H_2O$) or boric acid. It is further claimed for this mixture that if loaded into a cylindrical case with a constricted opening a non-instantaneous or "time" flash may be obtained.

The disadvantages of flashlight powders have been obviated by the introduction of the "*Sashalite*" bulb which produces a noiseless flash without smoke. As the flash takes place in the bulb, any danger of fire is eliminated, and for that reason it may be employed in positions where the use of ordinary flash powder would not be permissible.

The bulb is similar in appearance to an ordinary electric light bulb and is filled with oxygen at a low pressure. A low voltage filament is surrounded by finely beaten aluminium foil. When the current passes the foil is ignited, producing a flash of 1/75 of a second in duration. The current from a pocket torch-battery is sufficient for this purpose. A further advantage is that the electric ignition renders it independent of surrounding conditions, and it may be used under water, in wind, rain or snow.

Since the pyrotechnic possibilities of finely powdered aluminium have become known, the magnesium in most flash powders is usually partly, or even wholly, replaced by aluminium; one such mixture consists of:

Aluminium powder . . .	40 parts
Potassium perchlorate . .	60 „

It is usual, however, to retain some of the magnesium in order to ensure the necessary high actinic quality of the light emitted. Thus a typical mixture consists of:

Powdered magnesium . .	100 parts
Powdered aluminium . .	50 „
Ferric oxide	30 „
Copper carbonate . . .	30 „
Magnesium sulphate (dry) .	5 „

The following mixtures are claimed to be non-explosive and almost smokeless:—

(1) Powdered magnesium and aluminium (the quantity of aluminium usually varying from ¼ to ½ the amount of magnesium), mixed with peroxides of calcium, magnesium or manganese.

(2) Powdered magnesium and aluminium mixed with perboric acid or tungstic acid or their salts.

(3) Powdered magnesium and aluminium, with sulphate of cerium or thorium, or an alum. For example:

Powdered magnesium	8 parts
Powdered aluminium	2 „
Finely powdered, dry chrome alum .	10 „

Many mixtures containing aluminium as an ingredient are rendered more rapid in their combustion by the addition of silica, while their rate of combustion may be retarded by the introduction of regulated quantities of carbonates of alkalis or alkaline earths or oxides of the latter. Thus the above mixture may be converted into a slow-burning " time " mixture by the addition of 2 parts of an alkaline-earth oxide or carbonate.

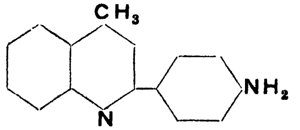
Flash powders are now frequently loaded into small cases or cartridges; ignition of the mixture being effected sometimes by an electric arrangement and sometimes by means of an inserted strip of magnesium ribbon. In the former case, the two electric wires are fixed into the cartridge, with either a short spark-gap or joined by a fine incandescing wire.

One of the many patented cartridges has a case which is itself inflammable. It consists of a short celluloid cylinder closed at the bottom with a cork saturated with collodion, and at the top with a disc of cork saturated with an emulsion of magnesium. Through this there is inserted a short strip of magnesium ribbon which, on ignition, starts the combustion of the charge.

A number of contrivances have been devised for producing a rapid succession of flash lights for purposes of cinematograph photography. These consist essentially of mechanical devices for the intermittent feeding of metallic magnesium against the two metal terminals of an electric circuit.

A. St. H. B.

FLAVANILINE, 2-*p*-aminophenyl-4-methylquinoline

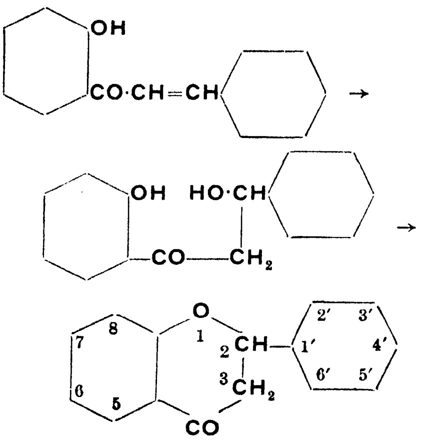


is formed by the action of zinc chloride on acetanilide at 250–270° (Fisher and Rudolph, Ber. 1882, **15**, 1500; G.P. 19766); by the action of acetic anhydride on aniline salts at 180–200° (G.P. 27948); by heating acetophenoneoxime at 60° with P_2O_5 (Goldschmidt, Chem.-Ztg. 1903, **27**, 279); and by usual methods from quinoline derivatives. Flavaniline has m.p. 97°, is sparingly soluble in water but dissolves readily in acids to give yellow-green solutions.

FLAVANONE or DIHYDROFLAVONE, I, is produced when 2-hydroxychalkone is digested at the boiling temperature with alcoholic mineral acid (v. Kostanecki and Szabrański, Ber. 1904, **37**, 2634), and this is the method generally adopted for the synthesis of flavanone derivatives. Flavanone is also readily obtained in 80% yield (Löwenbein, *ibid.* 1924, **57**, [B], 1515) by adding excess of aqueous sodium hydroxide (1–2%) to a warm alcoholic solution of *o*-hydroxychalkone.

On hydrolysis, the flavanones yield chalkones, a reversal of the reaction given above. The reaction in these cases is not unidirectional, and the conversion of flavanone into chalkone, or chalkone into flavanone, is never complete.

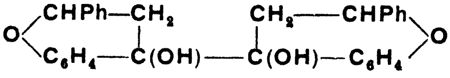
Though as a rule a chalkone only is obtained by the interaction of a hydroxyacetophenone and a benzaldehyde derivative, in certain instances the corresponding flavanone is directly produced. Thus, condensation of gallacetophenone dimethyl ether with benzaldehyde in presence of sodium hydroxide yields 7:8-dimethoxyflavanone (Woker, von Kostanecki, and Tambor, Ber. 1903, **36**, 4235).



I.

According to Shinoda and Sato (J. Pharm. Soc. Japan, 1928, **48**, No. 558, 109) who employed the method of Behn (Chem. Zentr. 1898, I, 1223), condensation of derivatives of cinnamoyl chloride with resorcinol in nitrobenzene solution in presence of aluminium chloride gives chalkones, whereas with phloroglucinol the main products are flavanone derivatives. For example, cinnamoyl chloride and resorcinol yield in this manner 2′:4′-dihydroxychalkone, whereas with phloroglucinol, 5:7-dihydroxyflavanone and 2′:4′:6′-trihydroxychalkone are obtained.

Flavanone crystallises in small colourless needles, m.p. 75–76°, and is reduced by aluminium amalgam in neutral alcoholic solution to flavanol (4-hydroxyflavane), m.p. 119° (corr.) (Freudenberg and Orthner, Ber. 1922, **55**, [B], 1748). The *pinacone*:



$$\mathrm{O}\left\langle\begin{array}{l}\mathrm{CHPh{-}CH_2}\\ \mathrm{C_6H_4{-}C(OH)}\end{array}\right.\left.\begin{array}{l}\mathrm{CH_2{-}{-}CHPh}\\ \mathrm{{-}C(OH){-}C_6H_4}\end{array}\right\rangle\mathrm{O}$$

is formed as a by-product. The reduction of flavanone with titanous chloride (Karrer, Yen and Reichstein, Helv. Chim. Acta, 1930, **13**, 1308) is said to yield the isomeric flavanols melting at 148–149° (corr.) and 120–120·5° (corr.), respectively, the latter evidently being the flavanol obtained by Freudenberg and Orthner (*l.c.*). A small amount of the corresponding pinacone is also obtained during this reaction.

Flavanones, flavones and flavonols can be distinguished by their behaviour on reduction (Asahina and Inubuse, Ber. 1928, **61**, [B], 1646). Thus, the hydroxyflavonols give red dyes only with magnesium and hydrochloric acid, the hydroxyflavones only with sodium amalgam, whereas the hydroxyflavanones react with both acid and alkaline reducing agents. Flavanone derivatives are reduced by sodium amalgam to the corresponding anthocyanidins; thus, *eriodictyol* (5:7:3′:4′-tetrahydroxyflavanone) yields *luteolinidin* when treated in this manner (Asahina, Nakagome and Inubuse, *ibid.* 1929, **62**, [B], 3016).

The existence of optically active flavanones has been observed by Fujise and Kubota (Ber. 1934, **67**, [B], 1905) and Fujise and Nagasaki (*ibid.* 1936, **69**, [B], 1893). *Matteucinol* and *demethoxymatteucinol*, isolated from *Matteucia orientalis*, are the only known optically active natural flavanones; these substances are completely racemised on short heating and yield compounds identical with synthetic 5:7-dihydroxy-6:8-dimethyl-4′-methoxyflavanone and 5:7-dihydroxy-6:8-dimethylflavanone, respectively. It is probable that many natural flavanones, hitherto obtained only in the *dl*-form, exist in the plant in optically active form and are racemised in the process of their isolation.

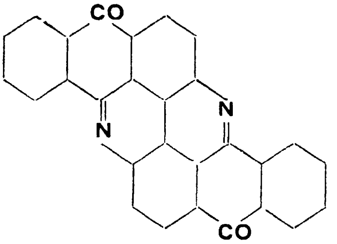
Ryan and Cruess-Callaghan (Proc. Roy. Irish Acad. 1929, **39B**, 124) prepared 3-arylideneflavanones by condensing flavanone and its derivatives with aromatic aldehydes in the presence of hydrogen chloride.

Flavanones are converted into flavones and flavonols by methods described under FLAVONE and FLAVONOL.

A. G. P. and E. J. C.

FLAVANTHRENE (*v.* Vol. I, 399*c*).

FLAVANTHRONE, *Indanthrene Yellow G*,



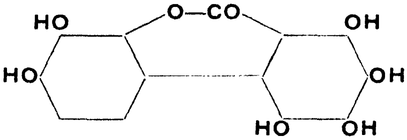
is the yellow compound obtained by heating 2-aminoanthraquinone with aluminium chloride or other catalysts of similar type, such as antimony halides, together with iodine (*cf.* U.S.P. 2062450). Flavanthrone has also been prepared by the action of ammonia at 230° on 2:2′-dibromo-1:1′-dianthraquinonyl (Schwenk and Waldmann, J. pr. Chem. 1931, ii, **130**, 79; *cf.* B.P. 336983) and by the action of sodium aluminium chloride at 235° on 2:2′-diphthalimidodiphenyl (Krepelka and Stefec, Coll. Czech. Chem. Comm. 1937, **9**, 29). It is the parent of the important series of flavanthrone vat dyestuffs (*v.* ANTHRAQUINONE DYESTUFFS, Vol. I, 412*d*).

FLAVASPIDIC ACID (*v.* FILIX MAS, this Vol. p. 181*c*).

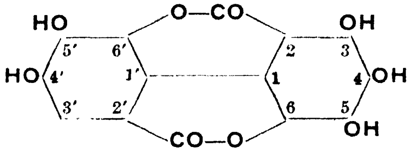
FLAVELLAGIC ACID, $C_{14}H_6O_9$, is obtained by oxidising a solution of gallic acid in dilute sulphuric acid with potassium persulphate at 50° (Perkin, J.C.S. 1906, **89**, 251), or by electrolytic oxidation of gallic acid in presence of sulphuric acid (A. G. Perkin and F. M. Perkin, *ibid.* 1908, **93**, 1194), or by heating gallic acid at 110–120° with arsenic and sulphuric acids (Bleuler and Perkin, *ibid.* 1916, **109**, 529).

Flavellagic acid crystallises from pyridine in small yellow prismatic needles which contain pyridine and do not melt below 360°. It dissolves in dilute alkalis with a yellowish-green coloration, and with nitric acid containing nitrous acid and subsequent dilution, it gives the blood-red coloration which is also produced by ellagic acid.

When distilled with zinc dust, flavellagic acid yields fluorene, whereas with boiling 50% potassium hydroxide solution hexahydroxydiphenylmethylolid:



is produced. Flavellagic acid is, therefore, hydroxyellagic acid (3:4:5:6:4′:5′:6′-heptahydroxydiphenyl-2:2′-dicarboxylic acid 2:6′:2′:6-dilactone):



(*cf.* Herzig and Tscherne, Monatsh, 1908, **29**, 281).

The following derivatives of flavellagic acid have been prepared: *Penta-acetyl*, colourless needles, m.p. 317–319°; *pentabenzoyl*, prismatic needles, m.p. 287–289° (Perkin, *l.c.*); and the *pentamethyl ether*, m.p. 245° (von Bronneck, Monatsh. 1908, **29**, 289). Oxidation of gallic acid 3:4-dimethyl ether, or gallic acid trimethyl ether, by means of potassium persulphate and sulphuric acid at 45° (Herzig and Schmidinger, *ibid.* 1910, **31**, 819), gives *flavellagic acid 4:5:4′:5′-tetramethyl ether*, yellow needles, m.p. 270–271°, the 3-*acetyl* derivative of which melts at 237–238°.

Flavellagic acid dyes mordanted woollen cloth shades somewhat resembling, but stronger than, those produced by ellagic acid:

Chromium.	Aluminium.	Tin.	Iron.
Yellowish-olive	Pale greenish-yellow.	Pale yellow.	Dark olive-brown.

A. G. P. and E. J. C.

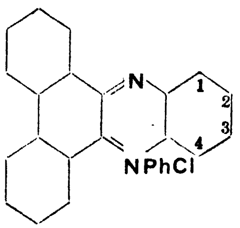
FLAVENOL, 2-*p*-*hydroxyphenyl*-4-*methylquinoline*, m.p. 238°, obtained from flavaniline by the diazo-reaction.

FLAVEOSIN (*v.* Vol. I, 133*c*).

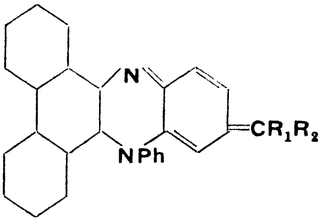
"**FLAVIANIC ACID.**" Name used by Kossel and Gross (Z. physiol. Chem. 1924, **135**, 168) for Naphthol Yellow S (1-naphthol-2:4-dinitro-7-sulphonic acid) (*v.* Vol. III, 417*d*).

FLAVIN. An important commercial preparation of quercitron-bark; *yellow flavin* consists essentially of quercitrin, while *red flavin* contains only quercitin.

FLAVINDULINE,



the chloride is formed by heating phentraquinone with *o*-aminodiphenylamine hydrochloride (G.P. 79570). According to Hantzsch (Ber. 1900, **33**, 291) the pseudo base must be formulated with hydroxyl on carbon atom 3 as condensation with compounds containing reactive methylene groups gives products of the type



Flavinduline salts themselves dye mordanted cotton yellow.

FLAVINDULINE O (*v.* Vol. I, 570*b*, 572*b*).

FLAVINE (*v.* Vol. I, 134*b*).

FLAVOGALLOL, $C_{21}H_8O_{12}$, is obtained by heating a solution of gallic acid in 80% sulphuric acid with arsenic acid at 120° for 6 hours (Bleuler and Perkin, J.C.S. 1916, **109**, 531). It forms hair-like yellow needles which carbonise without melting and are sparingly soluble in the usual solvents but soluble in sodium hydroxide solution with an orange-yellow colour.

By the action of sulphuric acid it yields the *anhydrosulphate*, $C_{21}H_6O_{11},H_2SO_4$, orange-yellow prisms; the *tripotassium* salt, $C_{21}H_5O_{12}K_3$, prepared with alcoholic potassium acetate, forms an orange-coloured crystalline powder. With boiling aniline, flavogallol yields the *anilide*, $C_{21}H_7O_{11}\cdot NH\cdot C_6H_5$, yellow needles, m.p. above 345°. *Hexabenzoylflavogallol* forms yellow prisms, m.p. 326–328°, and *hexa-acetylflavogallol*, small prismatic needles, melting at 278–280° (decomp.).

When hexa-acetylflavogallol is hydrolysed by means of acid in presence of ethyl or methyl alcohol, *ethyl flavogallonate*, $C_{23}H_{14}O_{13}$, pale yellow needles, or *methyl flavogallonate*, $C_{22}H_{12}O_{13}$, respectively, is produced. By gentle treatment with 30% potassium hydroxide solution, flavogallol yields *flavogallonic acid*, $C_{21}H_{10}O_{13}$, needles, m.p. above 300°, and this, when acetylated, is converted into acetylflavogallol.

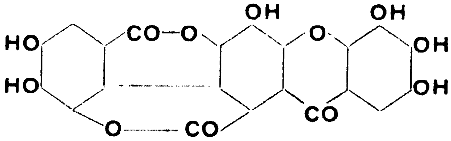
The more energetic action of potassium hydroxide solution gives *flavogallone*, $C_{20}H_{10}O_{11}$, minute needles, which with acetic anhydride forms the *acetyl* compound, $C_{34}H_{24}O_{18}$, leaflets, m.p. 257–259°.

When flavogallol is methylated with alkali and methyl sulphate and the product is digested with 5% potassium hydroxide solution, two apparently isomeric acids, $C_{21}H_4O_5(OMe)_{10}$, (*a*) colourless prisms, m.p. 206–208°, and (*b*), m.p. 238–240°, are obtained, and these both appear to be produced by the addition of 3 mol. of water to flavogallol and subsequent methylation of 10 hydroxyl groups. These acids give dimethyl esters of the formula:

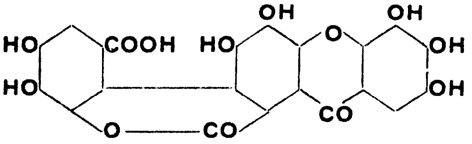
$$C_{29}H_{32}O_{11}(COOMe)_2$$

(*a*) melting at 128–130°, and (*b*) at 86–87°. The acid, m.p. 206–208°, loses one methoxyl group by digestion with alcoholic potash at 175° forming the *acid* $C_{28}H_{30}O_{11}(COOH)_2$, glistening leaflets, m.p. 183–184°.

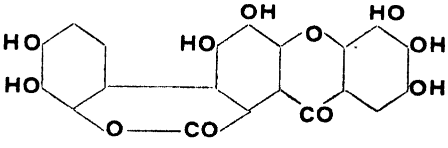
These reactions suggest the presence in flavogallol of an ellagic acid nucleus, and Bleuler and Perkin (*l.c.*) tentatively suggest the formula:



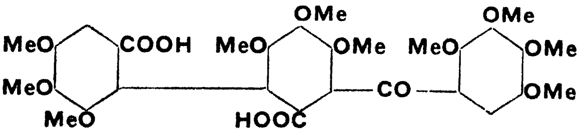
for this colouring matter. If this should prove correct, flavogallonic acid, flavogallone and the dicarboxylic acid, m.p. 206–208°, will possess structures (I), (II) and (III) respectively.



I.



II.



III.

Flavogallol yields the following shades on mordanted woollen cloth:

Chromium.	Aluminium.	Tin.	Iron.
Old gold.	Pale brownish-yellow.	Pale greenish-yellow.	Brownish-grey.

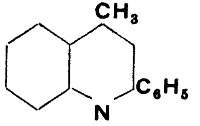
A. G. P. and E. J. C.

FLAVOGALLONE *v.* Flavogallol.

FLAVOGALLONIC ACID *v.* Flavogallol.

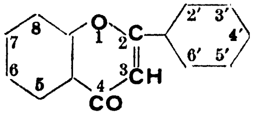
FLAVOGLAUCIN *v.* Fermentation, Mould (this Vol., p. 54*c*).

FLAVOLINE,



4-methyl-2-phenylquinoline (2-phenyllepidine), plates, m.p. 64–65°, b.p. 373–375°, is obtained by condensing acetophenone with *o*-aminoacetophenone in presence of alkali (Fischer, Ber. 1886, **19**, 1037).

FLAVONE, 2-phenylchromone:

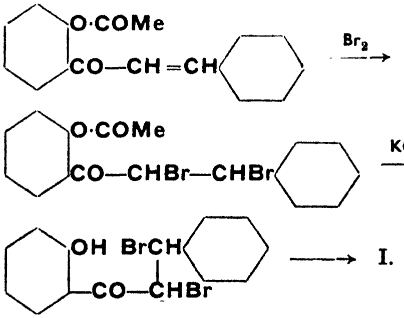


I.

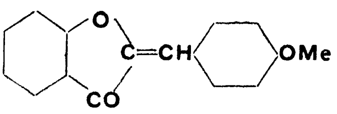
is the mother substance of a large and important group of colouring matters which are found widespread in nature.

Flavone and hydroxyflavones have been synthesised by the following methods:

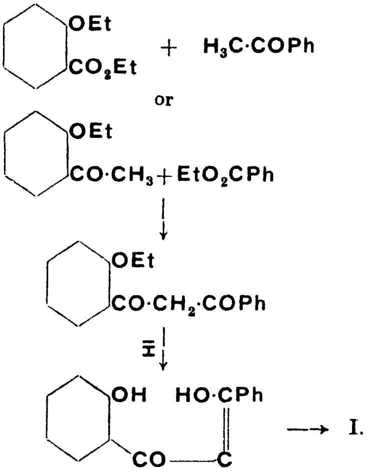
(1) By brominating *o*-acetoxybenzylideneacetophenones (*o*-acetoxychalkones) and treating the resulting *o*-acetoxyphenyl styryl ketone dibromides with alcoholic potash (Emilewicz and von Kostanecki, Ber. 1898, **31**, 696):



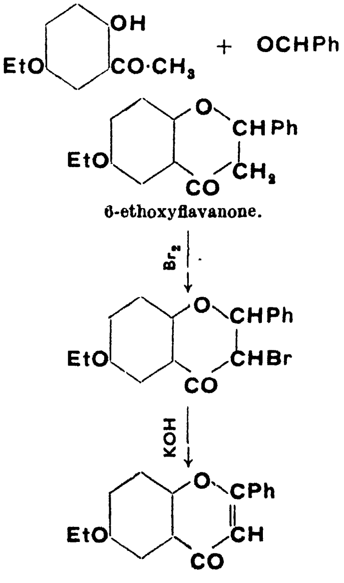
According to Auwers and Anschütz (*ibid.* 1921, **54** [B], 1543), an *o*-hydroxyphenyl styryl ketone dibromide may be converted into a flavone or a coumaranone by a suitable variation of the experimental conditions. For example, when cold aqueous sodium hydroxide is added to a suspension of 2-hydroxy- (or acetoxy-) phenyl 4-methoxystyryl ketone dibromide in alcohol, 4′-methoxyflavone is produced, whereas addition of alkali to the boiling solution gives 4′-methoxybenzylidenecoumaranone:



(2) Condensation of ethyl *o*-ethoxybenzoate with acetophenone, or *o*-ethyoxyacetophenone with ethyl benzoate, in presence of sodium yields *o*-ethoxybenzoylacetophenone; this compound, when digested with boiling hydriodic acid, gives flavone (von Kostanecki and Tambor, *ibid.* 1900, **33**, 330):



(3) *o*-Hydroxyacetophenone derivatives can be condensed with aromatic aldehydes with production of flavanones (dihydroflavones). These, with bromine, yield bromoflavanones which are converted into flavones with elimination of hydrobromic acid by treatment with alkalis (von Kostanecki, Levi and Tambor, *ibid.* 1899, **32**, 326), *e.g.*:



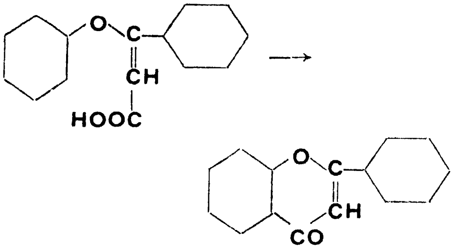
6-ethoxyflavanone.

(4) Dehydrogenation of flavanone with phosphorus pentachloride gives flavone (Löwenbein, *ibid.* 1924, **57** [B], 1515). This reaction has been applied by Hattori (Bull. Chem. Soc. Japan, 1927, **2**, 171) to the synthesis of substituted flavones.

(5) For the synthesis of flavones, Ruhemann (Ber. 1913, **46**, 2188) employed the esters of β-hydroxyarylcinnamic acids prepared by the interaction of esters of phenylpropiolic acid with sodium phenolates:

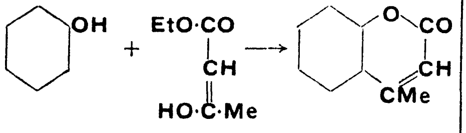
$$C_6H_5{\cdot}C{:}C{\cdot}COOR + NaO{\cdot}C_6H_5 = C_6H_5{\cdot}C(OC_6H_5){:}CNa{\cdot}COOR$$

These esters are readily transformed into the free acids, the chlorides of which yield the corresponding flavones when heated with aluminium chloride. Thus, flavone is produced in this manner from β-phenoxycinnamic acid:

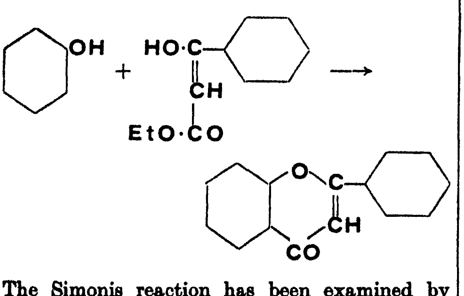


Chloroflavones have been prepared in a similar manner (Ruhemann, *ibid.* 1921, **54** [B], 912).

(6) von Pechmann and Duisberg (*ibid.* 1883, **16**, 2119) found that condensation of phenols with β-ketonic esters in presence of sulphuric acid yielded α-pyrone (coumarin) derivatives, *e.g.* the preparation of methylcoumarin from phenol and acetoacetic ester:



On the other hand, Simonis and co-workers (*ibid.* 1913, **46**, 2014; 1914, **47**, 692, 2229) obtained γ-pyrone (chromone) derivatives by employing phosphorus pentoxide as condensing agent. Thus, condensation of phenol and benzoylacetic ester in this way yields flavone:

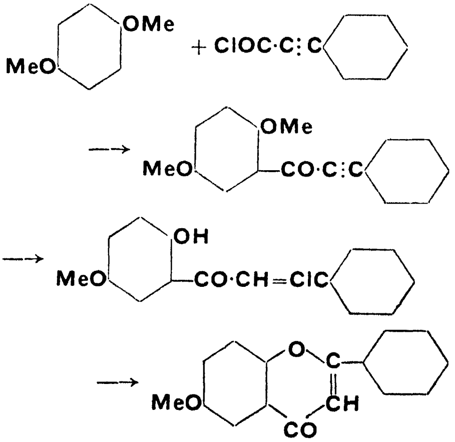


The Simonis reaction has been examined by Robertson and co-workers (J.C.S. 1931, 1255, 1877, 2426; 1932, 1180, 1681; Nature, 1931, **128**, 908) and Chakravarti (J. Indian Chem. Soc. 1931, **8**, 129, 407, 619; 1932, **9**, 25, 31, 389) who show that the reaction is not of general application. Chakravarti observes that only those phenols which react with difficulty or do not react at all with β-ketonic esters in presence of sulphuric acid to form coumarins, yield chromones in presence of phosphorus pentoxide.

Jacobson and Ghosh (J.C.S. 1915, **107**, 424, 959, 1051) and Ghosh (*ibid.* 1916, **109**, 105) claimed to have prepared benzo-γ-pyrones by condensing phenols with β-ketonic esters or nitriles in presence of condensing agents such as zinc chloride, sulphuric acid, or hydrogen chloride. These condensations, however, were shown by Baker and Robinson (*ibid.* 1925, **127**, 1981) and Baker (*ibid.* 2349) to lead to α-pyrone derivatives.

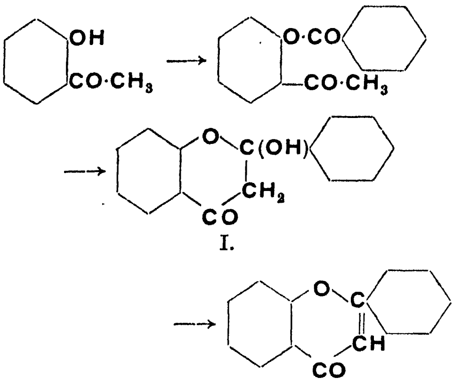
Again, the substance obtained by Meyer (J. pr. Chem. 1903, [ii], **67**, 342) by condensing benzoacetodinitrile with resorcinol in presence of hydrogen chloride, and considered by him to be 7-hydroxyflavone, was subsequently proved by Sonn (Ber. 1918, **51**, 821) to be the isomeric 7-hydroxy-4-phenylcoumarin.

(7) Simonis and Danischewski (*ibid.* 1926, **59** [B], 2914) synthesised chalkones, flavanones and flavones by an application of the Friedel-Crafts reaction. Thus, quinol dimethyl ether, phenylpropiolyl chloride and aluminium chloride in molecular proportions give 2:5-dimethoxyphenyl β-phenylethinyl ketone. This is converted by a further molecule of aluminium chloride into 2-hydroxy-5-methoxyphenyl β-chlorostyryl ketone, transformed by sodium hydroxide into 6-methoxyflavone:

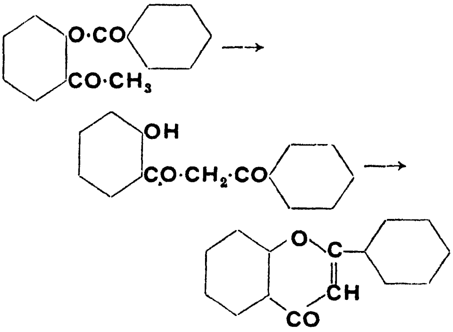


(8) Flavone and flavonol derivatives have been synthesised by Robinson and collaborators (J.C.S. 1924, **125**, 2192 *et seq.*) by aroylation of substituted *o*-hydroxyacetophenones. Thus, a mixture of resacetophenone, benzoic anhydride and sodium benzoate, when heated at 180–185°, gives a product from which 7-hydroxyflavone is obtained by hydrolysis. It is suggested by Baker (*ibid.* 1933, 1384) that the reaction proceeds through the following stages: (*a*) esterification of the phenolic hydroxyl group, (*b*) closure to a 2-hydroxyflavanone (I), and (*c*) loss of a

molecule of water with production of the flavone:



(9) Baker (*l.c.*) has shown that *o*-aroyloxyacetophenones, when heated with benzene or toluene and potassium carbonate, undergo intramolecular rearrangement yielding *o*-hydroxydibenzoylmethanes. These are converted into flavones by ring closure which probably proceeds through a 2-hydroxyflavanone (I) as shown above; it is also possible that (I) may be an intermediate during the migration of the benzoyl group. *o*-Benzoyloxyacetophenone by this method gives *o*-hydroxydibenzoylmethane, from which flavone is obtained by treatment with concentrated sulphuric acid:



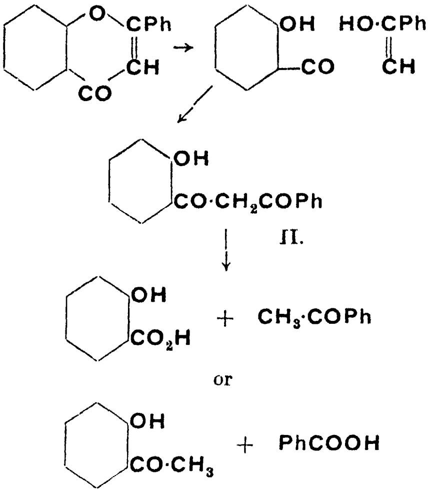
Migration of the benzoyl group also takes place in the presence of sodamide (Mahal and Venkataraman, J.C.S. 1934, 1767).

(10) *o*-Hydroxychalkones are converted into flavones by oxidation with selenium dioxide (Mahal, Rai and Venkataraman, *ibid.* 1935, 866).

Flavone crystallises from ligroin in colourless needles, m.p. 97°, and is readily soluble in the usual organic solvents. Its solution in sulphuric acid is yellow and possesses a weak blue fluorescence. The *oxime* melts at 237° (Gulati and Ray, Current Sci. 1936, **5**, 75).

Natural flavone occurs as the characteristic dust, termed by gardeners "meal" or "farina," which is present on the flower stalks, leaves and seed capsules of varieties of the primula, and is most pronounced on varieties obtained from China and Japan (Müller, J.C.S., 1915, **107**, 872).

Flavone and hydroxyflavones are hydrolysed by the action of alkalis; the first product of the reaction, owing to the disruption of the pyrone ring, is the β-diketone (II) which then suffers further hydrolysis according to the scheme:



The products of the hydrolysis of naturally occurring flavone colouring matters have been mainly instrumental in determining their constitutions.

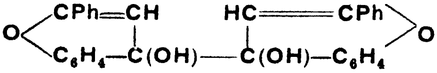
The absorption spectra of flavone and flavonol colouring matters have been studied by several workers. Shibata and Kimotsuki (Acta Phytochim. 1923, **1**, 91) observe that flavone colouring matters show two characteristic absorption curves in the ultra-violet, and since the position of these bands is affected by the number and orientation of the hydroxyl groups, the ultraviolet absorption spectra can be employed for identifying the different members of this series. Tasaki (*ibid.* 1925, **2**, 119) shows that the replacement of the hydroxyl groups of flavones by methoxyl produces no marked alteration in the absorption spectra. Hattori (*ibid.* 1928, **4**, 41, 63; 1932, **6**, 131) also concludes that methoxyl and ethoxyl groups are optically equivalent to the hydroxyl group, whereas the auxochromic influence of the latter is destroyed by acetylation. With flavonols, methylation of the hydroxyl group produces a marked alteration in the absorption spectra (Tasaki, *l.c.*), and it is suggested that the bathochromic effect produced by the introduction of the pyrone hydroxyl is due possibly to tautomerism, an α-diketone or *ortho*-quinonoid form being produced. Stabilisation of this hydroxyl group by methylation reverses the effect.

Tasaki (*ibid.* 1925, **2**, 129) has employed the absorption spectra as a means of determining the probable position of the sugar nucleus in flavone and flavonol glycosides. Hattori (*l.c.*), again, shows that the glycosidoxyl group is spectrographically equivalent to the hydroxyl group, whereas an acetoxyl group completely extinguishes the effect of the hydroxyl. The position of the glycosidic linking in compounds of this type may thus be determined by acetylating the glycoside and comparing the absorption curve of the product with those of the acetyl derivatives of the isomeric hydroxyflavones.

The position of the sugar group in flavone and flavonol glycosides may be determined by hydrolysing the completely methylated glycoside; the point of attachment of the sugar nucleus is indicated by the position of free hydroxyl group in the product. Thus, methylation of myricitrin and hydrolysis of the product yields myricetin 5:7:3′:4′:5′-pentamethyl ether, indicating that the rhamnose residue in the glycoside is in the 3-position.

According to Asahina and Inubuse (Ber. 1928, **61** [B], 1646), flavones, flavanones and flavonols can be distinguished by their behaviour on reduction. Thus, the hydroxyflavonols give red dyes only with magnesium and hydrochloric acid, the hydroxyflavones only with sodium amalgam, whereas the hydroxyflavanones react with both acid and alkaline reducing agents. Shinoda (J. Pharm. Soc. Japan, 1928, **48**, 35) describes the colour reactions of flavone, flavanone and flavonol derivatives on reduction with magnesium and hydrochloric acid in alcoholic solution. Reduction of flavone and flavanone derivatives with sodium amalgam gives the corresponding anthocyanidins, *e.g.* acacetin (5:7-dihydroxy-4′-methoxyflavone) is converted into acacetinidin in this manner (Asahina, Nakagome and Inubuse, Ber. 1929, **62** [B], 3016).

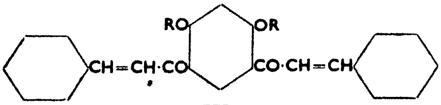
By reducing flavone with titanous chloride at the ordinary temperature, Karrer, Yen and Reichstein (Helv. Chim. Acta, 1930, **13**, 1308) obtained a small amount of the *pinacone*:



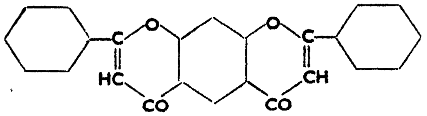
Bogert and Marcus (J. Amer. Chem. Soc. 1919, **41**, 83) prepared 2′-, 3′- and 4′-aminoflavones by nitrating flavone and reducing the mixed mononitro flavones.

Diflavone.

This substance was prepared by Ryan and O'Neill (Proc. Roy. Irish Acad. 1915, **32**, B, 48, 167) by interaction of benzaldehyde and diacetoresorcinol. The resulting dichalkone (III, **R**=**H**) yields the tetrabromide on bromination,



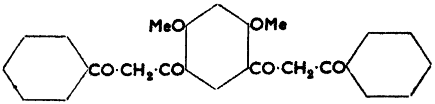
III.



IV.

and this is converted into *diflavone* (IV) by treatment with alcoholic potassium hydroxide.

The tetrabromide of 4:6-dibenzylidenediacetoresorcinol dimethyl ether (III, **R**=**Me**), when boiled with methyl-alcoholic sodium methoxide followed by boiling hydrochloric acid, yields dibenzoylacetoresorcinol dimethyl ether (V) from



V.

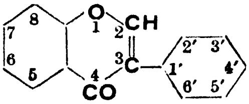
which diflavone is obtained by the action of hydriodic acid (Algar and Hanway, *ibid.* 1934, **42**, B, 9). Hydroxydiflavones are synthesised in a similar manner.

Employing the Allen-Robinson method, Wittig (Ber. 1926, **59** [B], 116) prepared 3:3′-dimethyldiflavone by benzoylation of 4:6-dipropionylresorcinol and treatment of the product with boiling dilute sodium hydroxide solution. Diflavones have been synthesised in a similar manner by Gulati and Venkataraman (J.C.S. 1931, 2376) and Algar, McCarthy and Dick (Proc. Roy. Irish Acad. 1933, **41**, B, 155).

Diflavone, pale yellow needles, m.p. 280–281°, resembles flavone in its general properties, and dissolves in concentrated sulphuric acid forming a yellow solution which exhibits a brilliant blue fluorescence. Natural colouring matters of this group are at present unknown.

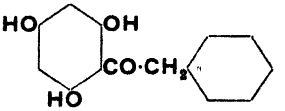
A. G. P. and E. J. C.

***iso*FLAVONE.** Whilst derivatives of flavone (2-phenylchromone) are found widespread in nature, few derivatives of *iso*flavone (3-phenylchromone):

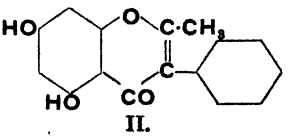


have, as yet, been isolated from natural sources. Although Finnemore (Pharm. J. 1910 [iv], **31**, 604) had suggested an *iso*flavone structure for prunetol, obtained from a variety of *Prunus* bark, it was not until Baker and Robinson (J.C.S. 1926, 2713) synthesised methylgenistein (methylprunetol dimethyl ether) that conclusive proof was afforded that *iso*flavone derivatives occur in nature.

*iso*Flavone derivatives have been synthesised by Baker and Robinson (*l.c.*; J.C.S. 1925, **127**, 1981; 1928, 3115; 1929, 152) by the interaction, at 170–180°, of derivatives of 2-hydroxyphenyl benzyl ketone with a mixture of the anhydride and sodium salt of an appropriate carboxylic acid, subsequently hydrolysing the product. For example, 2:4:6-trihydroxyphenyl benzyl ketone (I), acetic anhydride, and sodium acetate yield ultimately 5:7-dihydroxy-2-methyl-



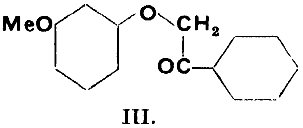
I.



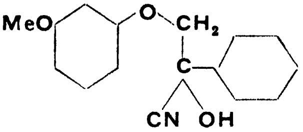
II.

*iso*flavone (II). The production of *iso*flavones unsubstituted in the 2-position is effected by employing cinnamic anhydride and sodium cinnamate in this reaction, or by condensing a 2-methyl*iso*flavone with benzaldehyde (Baker, Robinson and Simpson, *ibid.* 1933, 274). The 2-styryl*iso*flavone derivatives thus obtained are converted by oxidation into *iso*flavone-2-carboxylic acids which are decarboxylated on heating with formation of *iso*flavones.

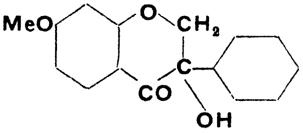
A method applicable to the synthesis of derivatives of 7-hydroxy*iso*flavone is described by Baker, Pollard and Robinson (*ibid.* 1929, 1468). ω-*m*-Methoxyphenoxyacetophenone (resorcinol methyl phenacyl ether) (III) readily yields the cyanhydrin (IV), and this, when treated with zinc chloride and hydrogen chloride in ethereal solution, undergoes cyclisation to the ketimine hydrochloride which on hydrolysis yields 3-hydroxy-7-methoxy*iso*flavanone (V), and this forms 7-methoxy*iso*flavone (VI) when dehydrated with cold concentrated sulphuric acid. This method, however, fails in certain cases either because the cyanohydrin cannot be obtained or because the ring closure in the second stage cannot be effected (Baker, Morgans and Robinson, *ibid.* 1933, 374).



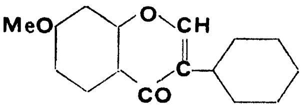
III.



IV.

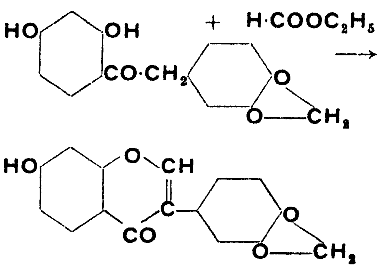


V.



VI.

Späth and Lederer (Ber. 1930, **63** [B], 743) prepare *iso*flavone derivatives by heating *o*-hydroxyphenyl benzyl ketones with ethyl formate and sodium at 100° in sealed tubes. The products, when treated with alcohol and fuming hydrochloric acid and sublimed in a high vacuum, yield *iso*flavones in small amount. Thus, 2:4-dihydroxyphenyl 3:4-methylenedioxybenzyl ketone (ψ-baptigenitin) gives 7-hydroxy-3′:4′-methylenedioxy*iso*flavone (ψ-baptigenin) when treated in this manner:



According to Venkataraman and co-workers (J.C.S. 1934, 513, 1120, 1769), however, excellent yields may be obtained by the action of sodium on solutions of *o*-hydroxyphenyl benzyl ketones in ethyl formate at a low temperature.

The following derivatives of *iso*flavone have been isolated from natural sources:

Daidzein, 7:4′-dihydroxy*iso*flavone, present as *daidzin* (daidzein 7-glucoside) in the Soya bean (*Soja hispida*) (Walz, Annalen, 1931, **489**, 118; Wessely, Kornfeld and Lechner, Ber. 1933, **66** [B], 685; Baker, Robinson and Simpson, *l.c.*; Mahal, Rai and Venkataraman, J.C.S. 1934, 1769).

Formononetin, 7-hydroxy-4′-methoxy*iso*flavone, from the glucoside *ononin* (probably daidzin methyl ether) found in the root of the spring rest-harrow, *Ononis spinosa* L. (Wessely and Lechner, Monatsh. 1931, **57**, 395; Wessely, Kornfeld and Lechner, *l.c.*; Wessely, Lechner and Dinjaški, Monatsh. 1933, **63**, 201; Mahal, Rai and Venkataraman, *l.c.*; *see also* Baker, Robinson and Simpson, *l.c.*).

Genistein (*prunetol*), 5:7:4′-trihydroxy*iso*flavone, which occurs with luteolin in Dyer's Broom (*q.v.*), and as *genistin* (genistein 7-glucoside) in *Soja hispida* (Walz, *l.c.*); *prunetin* (genistein 7- or 4′-methyl ether) obtained from the glucoside *prunitrin* present in *Prunus* bark (Finnemore, *l.c.*; Baker and Robinson, *l.c.*).

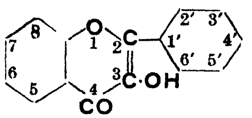
ψ-Baptigenin, 7-hydroxy-3′:4′-methylenedioxy*iso*flavone, from *ψ-baptisin*, a 7-rhamnoglycoside, isolated from the root of *Baptisia tinctoria* (Gorter, Arch. Pharm. 1897, **235**, 494; Späth and Schmidt, Monatsh. 1929, **53**, 454; Späth and Lederer, *l.c.*; Mahal, Rai and Venkataraman, *l.c.*; Baker, Robinson and Simpson, J.C.S. 1937, 805).

Tectorigenin, probably 5:7:4′-trihydroxy-6-methoxy*iso*flavone, present as the glycoside *tectoridin* in the rhizome of *Iris tectorum* Maxim (Shibata, J. Pharm. Soc. Japan, 1927, No. 543, 61; Asahina, Shibata and Ogawa, *ibid.* 1928, **48**, 150).

Irigenin, 5:7:3′-trihydroxy-6:4′:5′-trimethoxy*iso*flavone, from *iridin* (irigenin 7-glycoside) obtained from "Florentine Orris Root" (*Iris germanica*, *Iris pallida* and *Iris florentina*) (Baker, J.C.S. 1928, 1022; Baker and Robinson, *ibid.* 1929, 152; Shinoda and Sato, J. Pharm. Soc. Japan, 1932, **52**, 139).

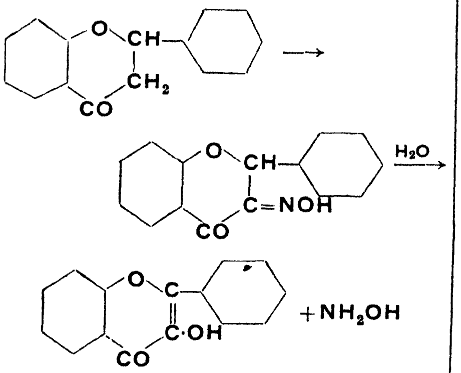
A. G. P. and E. J. C.

FLAVONOL. Derivatives of flavonol, 3-hydroxyflavone: form an important subdivision of the large group of yellow colours derived from flavone.

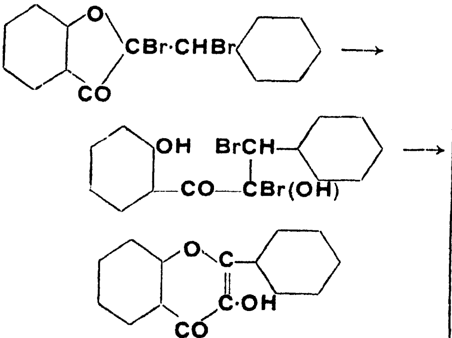


For the synthesis of flavonol and its derivatives the following general methods have been employed:

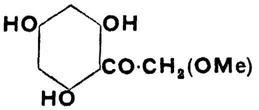
Treatment of flavanones with amyl nitrite and hydrochloric acid in alcoholic solution yields *iso*nitrosoflavanones, and these are converted into flavonols with elimination of hydroxylamine by boiling with dilute acids (von Kostanecki and Szabrański, Ber. 1904, **37**, 2819):



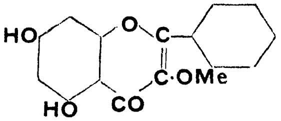
According to Auwers and Müller (*ibid.* 1908, **41**, 4233), flavonols are produced by heating the dibromides of benzylidenecoumaranones with alcoholic potassium hydroxide. The reaction probably proceeds according to the scheme:



Robinson and his co-workers (J.C.S. 1924, **125**, 2192; *et seq.*) have synthesised flavonols by aroylation of substituted ω-methoxy- (or ω-benzoyloxy-) *o*-hydroxyacetophenones. For example, a mixture of ω-methoxyphloracetophenone (I), sodium benzoate and benzoic anhydride, when heated to 180°, yields a product from which 5:7-dihydroxy-3-methoxyflavone (galangin monomethyl ether) (II) is obtained by hydrolysis.

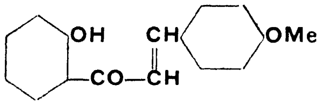


I.



II.

By treating *o*-hydroxyphenyl styryl ketones dissolved in hot alcoholic potassium hydroxide with hydrogen peroxide, Algar and Flynn (Proc. Roy. Irish Acad. 1934, **42B**, 1) obtained flavonols in good yields. Thus, *o*-hydroxyphenyl 4-methoxystyryl ketone (III) yields 4′-methoxyflavonol (IV) when treated in this manner. These authors suggest that the first stage of the oxidation is possibly the formation of a transitory ethylene peroxide: which would probably yield the flavonol by ring closure. The reaction might also be explained by assuming the formation of a glycol as intermediate product. On the other hand, Oyamada (J. Chem. Soc. Japan, 1934, **55**, 1256), who prepared flavonols in a similar manner, considers that the *o*-hydroxychalkone is first isomerised to the flavanone which is then oxidised to the flavonol: this conclusion is supported by the observation that *o*-hydroxychalkone yields flavanone with alkali alone, and flavanone is converted into flavonol by means of alcoholic hydrogen peroxide. According to Murakami and Irie (Proc. Imp. Acad. Tokyo, 1935, **11**, 229), *o*-hydroxychalkone in methyl alcohol is converted by alkali (2*N*-sodium hydroxide, triethylamine, or dilute aqueous ammonia) and hydrogen peroxide at room temperature into a mixture of flavonol and dihydroflavonol, the latter being the main product. Flavanone is oxidised by these reagents to flavonol.



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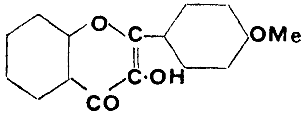

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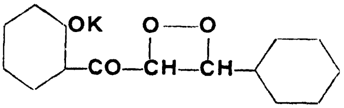
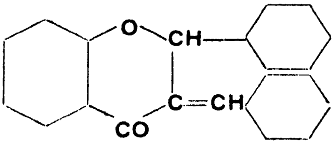


Whereas Algar and Flynn (*l.c.*) obtained flavonols in very small yields by treating 3-

arylideneflavanones (flavindogenides) with alkaline hydrogen peroxide, Algar and Carey (Proc. Roy. Irish Acad. 1937, **44B**, 37) found that by oxidation with potassium permanganate in presence of sulphuric acid 3-hydroxy-3-aroylflavanones are produced, and these are converted into the corresponding flavonols by mild treatment with alcoholic potassium hydroxide, both hydrolysis and oxidation apparently taking place. Thus, 3-benzylideneflavanone (V) in this manner affords 3-hydroxy-3-benzoylflavanone (VI) from which flavonol and benzoic acid are obtained by the action of alcoholic potassium hydroxide.



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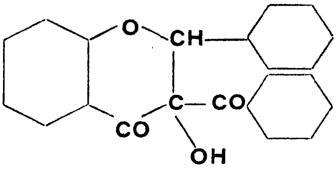
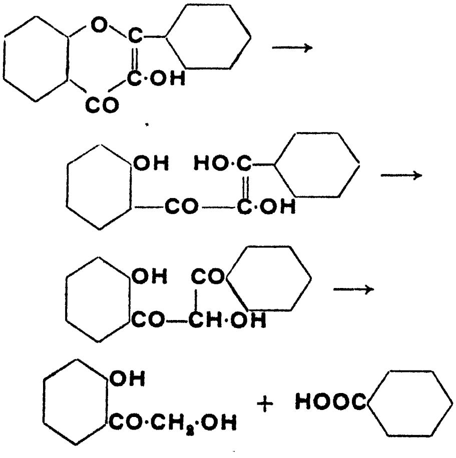


VI.

Flavonol crystallises from alcohol in yellow needles, m.p. 169–170° (von Kostanecki and Szabrański), m.p. 171–172° (Algar and Flynn), and dissolves in sulphuric acid forming a solution which exhibits an intense violet fluorescence. It yields an *acetyl* derivative, colourless needles, m.p. 110–111° (von Kostanecki and Szabrański), and a *methyl ether*, m.p. 114° (Oyamada).

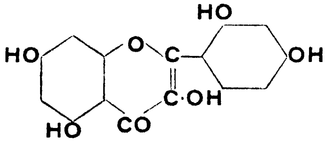
The hydrolysis of flavonol into *o*-hydroxybenzoylcarbinol and benzoic acid may be expressed by the following scheme:



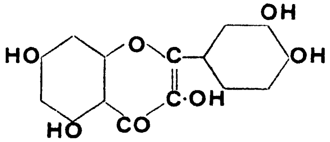
and this reaction, which is typical of the whole series of these compounds, has generally been employed to ascertain their structure. It is best effected by digesting the fully methylated flavonols with boiling alcoholic potassium hydroxide for some hours, for owing to the occurrence of secondary reactions it cannot be satisfactorily carried out with the unmethylated compounds.

The flavonols, with the exception of morin which curiously enough is colourless, are yellow crystalline substances soluble in alkaline solutions with a yellow colour, and yield orange crystalline oxonium salts with ease in the presence of acetic acid. According to Perkin hydroxyflavones, as a rule, are not oxidised by air in alkaline solution and can be precipitated therefrom unchanged by acids, whilst flavonols, on the other hand, are readily decomposed in this manner with the formation of water-soluble products.

The dyeing properties of the hydroxyflavonols appear to be due to the presence of the pyrone hydroxyl group, the effect of which is considerably strengthened by the presence of hydroxyls in other positions in the molecule, and this has received support from the observation of von Kostanecki and Szabrański that flavonol itself dyes on aluminium mordant a pale yellow shade. The effect of the pyrone hydroxyl is also very evident on comparing quercetin (VIII) which gives a brown-orange shade on aluminium mordant with luteolin (IX) which yields in the same way only a bright yellow colour.



VII.



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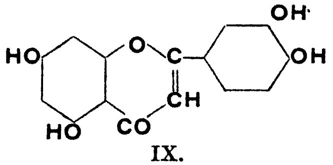


IX.

Though the presence of two hydroxyl groups in the *o*-position relatively to one another is not essential to the dyeing property of hydroxyflavonols, their presence, at least in certain positions, has considerable influence, not only in deepening the tone, but also in reddening the shade. This is clear from a comparison of morin (VII) and quercetin (VIII) which give yellow and brown-orange shades, respectively, on aluminium mordant.

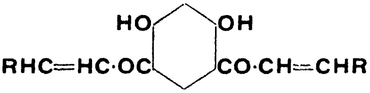
The shade given by a hydroxyflavonol glycoside is naturally dependent on the position of the sugar nucleus, and thus quercimeritrin (quercetin-7-glucoside) has quite distinct properties in this respect from quercitrin (quercetin-3-rhamnoside).

For an account of the absorption spectra of flavonols and flavonol glycosides, and of the method of determining the position of the sugar group in the latter, *see* FLAVONE.

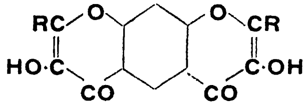
According to Asahina and Inubuse (Ber. 1928, **61** [B], 1646), flavones, flavanones, and flavonols can be distinguished by their behaviour on reduction (*see* FLAVONE). The reduction of a flavonol to the corresponding anthocyanidin was first accomplished by Willstätter and Mallison (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1914, **12**, 769) who obtained a very small yield of cyanidin chloride by reducing quercetin in methyl-alcoholic hydrochloric acid with magnesium and mercury. Interesting also is the fact that Freudenberg and Kammüller (Annalen, 1927, **451**, 209) prepared *dl*-epicatechin pentamethyl ether (*see* CATECHU or CUTCH) from quercetin pentamethyl ether by catalytic reduction.

Diflavonol.

Algar and Hurley (Proc. Roy. Irish Acad. 1936, **43**B, 83) were unsuccessful in their attempts to synthesise diflavonol by the methods employed by von Kostanecki and Szabrański, Auwers and Müller, and Robinson, for the synthesis of flavonols. Following the method of Algar and Flynn, however, dichalkones of the type (X; $R=C_6H_5$, etc.) were converted into diflavonols (XI) by treating a suspension of the dichalkone in aqueous-alcoholic sodium hydroxide with hydrogen peroxide in the cold.



X.



XI.

Diflavonol crystallises from boiling *cyclo*hexanone in yellow prisms, m.p. 323°, and gives a brown coloration with alcoholic ferric chloride. Its yellow solution in concentrated sulphuric acid exhibits a green fluorescence on standing. *Diacetyldiflavonol* forms colourless needles, m.p. 252°.

A. G. P. and E. J. C.

FLAVOPHOSPHINE (*v.* Vol. I, 133*b*).

FLAVOPURPURIN (*v.* Vol. I, 224*c*).

FLAVORHODIN. Flavorhodin occurs in minute quantity, together with several other carotenoid pigments, in a species of purple bacteria. The separation of pigments was effected by partition and chromatographic methods. Flavorhodin separates from alcohol in yellow crystals, m.p. 111–113°; it is epiphasic and exhibits absorption maxima at 5,030, 4,720 and 4,410Å (in carbon disulphide) (Karrer and Solmssen, Helv. Chim. Acta. 1935, **18**, 1306; Karrer, Solmssen and Koenig, *ibid.* 1938, **21**, 454).

I. M. H. and F. S. S.

FLAVOXANTHIN (*see* CAROTENOIDS). A xanthophyll, $C_{40}H_{56}O_3$, obtained from the yellow sepals of the buttercup (*Ranunculus acer*) in which it occurs in admixture with other xanthophylls and xanthophyll esters. Isolation of flavoxanthin was effected by partition and chromatographic methods. It separates from methyl alcohol in golden prisms, m.p. 184° (vac.), $[\alpha]^{20°}_{Cd}+190°$ (benzene). Flavoxanthin was identified as a trihydroxy-carotenoid by analysis, active hydrogen determination and by its light-absorption properties. In ethereal solution with 20% hydrochloric acid it gives a pale blue coloration (Schunck, Proc. Roy. Soc. 1903 **72**, 165; Karrer and Notthafft, Helv. Chim. Acta, 1935, **15**, 1195; Kuhn and Brockmann, Z. physiol. Chem. 1932, **213**, 192).

I. M. H. and F. S. S.

FLAX *v.* FIBRES, VEGETABLE (this Vol., p. 159).

FLAX WAX. Flax fibre is coated with a wax of which 2·5% (on the weight of fibre) can be recovered by extraction: 6–10% of wax can be obtained from the " pouce " or dust separated from flax fibre in the combing or drawing processes (Gibson, Trans. Inst. Chem. Eng. 1931). The wax is dark green or brown; it has a higher melting-point (67·3–69·5°C.) and is harder than beeswax and takes a high polish. The wax contains *phytosterol* and *ceryl alcohol*. It has d^{15} 0·963–0·985; saponif. value 78·4–83·7; iodine value 21·6–28·8; and acid value 17·5–23·8 (Honneyman, Pharm. J. 1926, **117**, 157).

FLEITMANN'S TEST (*v.* Vol. I, 470*b*).

FLEMINGIN, $C_{12}H_{12}O_3$. A yellow colouring matter present in *waras*, the resinous powder which covers the seed pods of *Flemingia congesta* Roxb., it is an orange-red crystalline powder, m.p. 171–172°, and on fusion with alkali yields salicylic and acetic acids (A. G. Perkin, J.C.S. 1898, **73**, 660).

FLINT. (Fr. *Silex*; Ger. *Feuerstein.*) A native form of silica, being a compact massive variety of the mineral quartz with some admixed hydrated silica (opal). It grades into chalcedony, chert, hornstone or jasper, and may be banded and marked like agate; no sharp line of demarcation can be drawn between these several varieties of quartz. The term " flint " is commonly limited to the nodular masses found in, or derived from, the Chalk formation. This material is of organic origin, being derived from the siliceous (opaline) remains of marine organisms (sponges with siliceous spicules, *radiolaria* and *diatomaceæ*) deposited on the sea-floor together with the calcareous remains of other organisms which gave rise to the chalk itself. After deposition, this disseminated siliceous material became segregated into nodules; being no doubt redeposited in the colloidal condition, and subsequently dehydrated and transformed into the crystalline condition. The fact that nodules of flint are usually arranged along the bedding planes in the chalk would suggest that these layers correspond to periods when siliceous organisms predominated, and that the solution and redeposition of the silica took place contemporaneously in the soft ooze. On the other hand, the occurrence of flint in platy forms filling vertical joints in the chalk, suggests that solution and redeposition may also have taken place subsequent to the consolidation of the chalk.

Flint is dull in colour and lustre, being yellowish, blackish, or more usually of a smoke-grey colour, and with a more or less waxy or greasy appearance. It breaks with a smooth conchoidal fracture, and under certain conditions with a conical fracture. Thin flakes are translucent at the edges. Thin sections in polarized light show that a large part of the material is minutely crystalline (crypto-crystalline). Sp.gr. 2·60–2·63 (somewhat less than that of crystallised quartz). The material consists of nearly pure silica (about 98%) with 1–1·4% of water, and traces of iron, aluminium, calcium and organic matter. It is much more readily soluble in a hot solution of caustic alkali than is crystallised quartz. The white patina or crust often seen on flints consists in some cases of adhering chalk mixed with silica ($CaCO_3$ 50%); or more often it consists wholly of silica, and has been produced by the weathering of the material, the opal being dehydrated or removed in solution and the crystalline particles liberated in a powdery condition. Analysis of flint pebbles from Knockmill, Kent, reduced to a white powder shows 97·43% SiO_2 (G. W. Himus, Proc. Geol. Assoc. 1936, **47**, 248).

Flints occur principally in the Upper Chalk, which is of wide distribution in the south-east of England, around the Paris basin, in Denmark, the island of Rügen, Co. Antrim, etc. With the denudation of the rock the resistant flints accumulate in gravels and other secondary deposits. The material is obtained: (1) as irregular nodules coated with chalk as a by-product from chalk quarries worked for lime, cement, whitening, etc.; (2) iron-stained pebbles from gravel pits; (3) boulders and pebbles collected on the sea-shore.

Flint was perhaps the very first mineral to be worked for practical uses, as witness the prehistoric palæolithic implements and the highly finished flints of the neolithic period. Flints for tinder-boxes and gun-flints are still worked by the flint-knappers at Brandon in Suffolk (for an account of this industry, *v.* S. B. J. Skertchly, Mem. Geol. Survey, 1879). Apart from the local use of flint as a building stone (*v.* E. T. Baggallay, Trans. R. I. Brit. Arch. 1885) and for road making and concrete, the principal use of the material is in the ceramic industry. For this purpose large quantities are collected along the French coast between Havre and St. Valery at the mouth of the Somme. The material is burnt and thrown into cold water, when it can readily be finely ground to a snow-white powder; large quantities of flint pebbles are also ground between blocks of chert. For the manufacture of porcelain, as well as for glazing and enamelling, powdered flint is better than crystallised quartz, probably on account of the difference in texture of the material. Formerly it was also used in the manufacture of glass (hence the term flint-glass). Powdered flint bonded with a highly plastic clay is used for making refractory silica-bricks for steel furnaces. Round nodules of flint are used in tube mills for grinding felspar, cement-clinkers, ore, etc., the silica worn from them being a non-injurious contamination. The Danish flints are best suited for this purpose. As an inert material it is used as a filler in acid towers. Powdered flint is used for making sand-paper. Flint is also cut and polished for use as agate-mortars, polishers and burnishers. (*v.* W. Hill, Flint and Chert, Proc. Geol. Assoc. 1911, **22**, 61; J. W. Mellor and A. J. Campbell, Flint and Quartz, Trans. English Ceramic Soc. 1916, **15**, 76; K. P. Oakley, Sci. Progress 1939, **34**, 277).

L. J. S.

FLOCONS *v.* Bleaching (Vol. II, 18*a*).

FLORENCITE. Basic phosphate of aluminium and cerium (Ce_2O_3, etc., 28%)—

$$AlPO_4{\cdot}CePO_4{\cdot}Al(OH)_3,$$

crystallised in the rhombohedral system and isomorphous with the strontium salt *hamlinite.* Sp.gr. 3·586. It is found as small yellowish grains and crystals in diamond-bearing sands near Diamantina, Brazil, and in cinnabar-bearing sands and in mica-schist with topaz near Ouro Preto, Brazil.

L. J. S.

FLORES CINAE, Santonica, wormseed. The dried unexpanded capitula of *Artemisia cina* Berg (fam. compositæ). Contains 2–3·5% of santonin..

FLORIBUNDINE, FLORIPAVINE, FLORIPAVIDINE. Opium alkaloids from *Papaver floribundum.*

"FLORICINEOL" (*v.* Vol. II, 422*b*).

"FLORIDEAN STARCH" *v.* Algæ (Vol. I, 200*d*).

FLORIDITOL *v.* Algæ (Vol. I, 200*d*).

FLORIDOSE *v.* Algæ (Vol. I, 200*c*).

FLORIDOSIDE *v.* Algæ (Vol. I, 200*d*).

"FLOSAL" (*v.* Vol. I, 363*a*).

FLOS-FERRI *v.* Aragonite.

FLOTATION PROCESS. By the "flotation process" is now meant that froth flotation process for cleaning or washing metalliferous ores, non-metallic minerals and coal which employs aeration, agitation and generally less than one-tenth per cent. by weight of oils or other substances soluble or insoluble in water, as the case may be.

In the treatment of a metalliferous ore, for example, some of these substances or reagents are added primarily to cause certain constituents of the crushed ore, generally the valuable mineral, to float in the froth produced by the aeration and agitation; these reagents are termed "collectors," or, less happily by many, "promotors." Other reagents termed "depressants" and "gangue modifiers" are added to make the remaining constituents sink. Reagents called "frothers" may be necessary to control the amount, stability and bubble size of the froth, whilst, if it is desired to refloat any of the depressed constituent minerals, reagents called "activators" are added subsequently.

In practice the amount of a reagent used is expressed in decimals of a pound (avoidupois) per ton of ore treated, for example "0·1 lb. of xanthate per ton" is equivalent to 0·005% by weight of the ore treated if the short ton of 2,000 lb. be employed; if 4 tons of water were used per ton of ore the strength of the xanthate solution employed would be approximately 0·001%, more exactly 1 part in 80,000 if the xanthate remained in solution.

For research work it is sometimes more convenient to compute the strength of reagents in terms of milligrams of reagent per litre of water for the given ore-water ratio, pulp ratio or pulp density used in the test, *e.g.* 12·5 mg. xanthate per litre in the above case. With some reagents as little as 2 mg. per litre, 1 part in 500,000 is used.

From a consideration of these quantities it is apparent that the flotation process consists of floating off particles of mineral attracted to the surfaces of the bubbles, the air–water interfaces, of a froth and not to any buoyancy effect of the reagents which attach themselves to the particles " floated."

The Principles.

Flotation depends fundamentally on the tendency of all dry insoluble freshly crushed minerals, metallic or non-metallic, to float when placed on the surface of water, *i.e.* to adhere to a gas-liquid interface. In the flotation process the surfaces of bubbles in water or in a froth provide a more adequate amount of gas-liquid interface for the collection of minerals than would the surface of a flowing stream of water. This tendency to float results from the fields of force, unbalanced attractions, which occur at the surfaces of liquids and solids in air, effects of surface tension and surface energy, more precisely the tensions at the gas-liquid and gas-solid interfaces, but, as the solid particles are at least partly wetted, there is a third force, the tension at the liquid-solid interface to be considered. The existence of the interfacial tensions and their relative strengths is shown by the contact angle θ made at the junction of the gaseous liquid and solid phases when drops of liquid are in equilibrium on a smooth horizontal solid surface in a gas (Fig. 1), or when a bubble of gas is in equilibrium on a similar solid surface in a liquid.

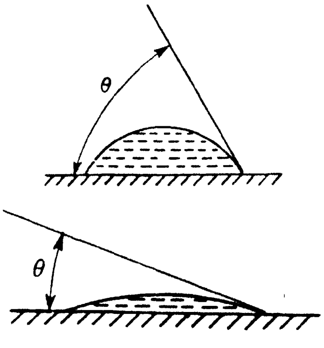


Fig. 1.

With air, water and a mineral the contact angle depends on the nature and state of the mineral surface and is a measure of the floatability of the mineral.

If the solid–liquid interfacial tension is high the contact angle will be low, as the solid–liquid interfacial tension is a measure of the tenacity of adhesion between the mineral and the water, the instability of the froth and the lack of floatability of the mineral in the flotation process. Conversely a high contact angle (Fig. 2) results from a low solid–liquid interfacial tension and indicates tenacity of adhesion between mineral and air, floatability. In practice there is a certain range of contact angle, called the hysteresis of the contact angle, which results when a drop of water is dragged along a mineral surface or the surface is inclined. This hysteresis is not the true measure of floatability.

The froth-flotation separation process depends (1) on the enhancement of floatability in the case of minerals it is desired to float off in the air-water froth produced, and (2) on the reduction of floatability in the case of minerals it is desired to sink by rendering them more readily wetted, less air-avid and less water-repellant. The interfacial tension between the mineral to be floated and the water has been increased as shown by the decreased contact angle. In an ore containing several different sulphide minerals it is necessary to collect each mineral separately in as pure a state as possible because of the demands of the smelter. This separation requires an accurate control of the wettability or non-wettability of each mineral in the ore and is now generally obtained by the use of reagents which, on dissociation in dilute solutions, yield suitable polar or polar-non-polar ions which are selectively adsorbed to the surfaces of the minerals it is desired to float or sink.

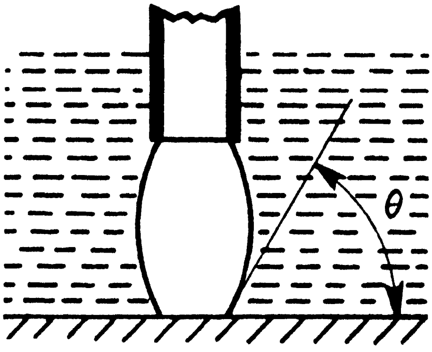


Fig. 2.

How considerable this control may be is well illustrated by the flotation of coal high in ash to remove the ash, and the subsequent sinking of the recovered coal to remove its pyritic content by flotation.

The first necessary condition for successful flotation is that flocculation must not be allowed to interfere with the selective attachment of the collected mineral to the air bubbles. Sometimes it is necessary to add deflocculating or dispersing reagents to the " pulp " (mixture of water and crushed ore) to prevent such flocculation.

Solid–solid adsorption of any gangue constituents to the sulphides it is desired to float must also be prevented, otherwise they will be coated with a wettable non-floatable layer. Precautions against this are only necessary in certain cases where primary slime, *e.g.* of clay or hæmatite, occurs in the ore. These may have to be removed by preliminary washing instead of being dealt with by reagents. Adequate deflocculation is thus the first necessary condition after adequate grinding.

The second necessary condition for successful flotation is that there should be adequate aeration of the pulp to give enough froth to supply a sufficient area of air–water surface for the collection of all the valuable mineral present; the mineral must not be crowded out of the froth. The formation of such a froth is assisted by the addition of a frothing agent or " frother," generally a soluble substance which reduces the surface tension of the water but does not introduce reactive ions into the pulp; pine oil and cresylic acid are the most widely used.

If the agitation is excessive the coarser particles may not be able to adhere sufficiently strongly to the bubbles to be collected; in rare cases where collection depends on a differential filming by a chemical compound, rather than by adsorption of ions, as in the differential flotation of an oxidised lead and zinc ore by sodium taurocholate, the coating may actually be rubbed off by too violent agitation although all the other conditions for flotation are correct. This can be avoided by reducing the speed of the impeller and thus the violence of the agitation.

An excessive area for the collection of the froth may result in the froth being too weak because there is not enough mineral to armour the bubbles and thus render them strong enough not to break and drop their load before removal from the cell.

Some managers have nearly closed down their mines by insisting on more agitation and bigger and bigger cells when recovery was poor, thus getting a weaker and weaker froth. If correctly chosen reagents are used, loss should be avoidable by the use of crowding boards, to reduce the area of the cells.

The third necessary condition for successful flotation is that the froth produced should be sufficiently stable (tough) to allow of its removal from the cell, or flotation machine, without undue loss of floated mineral by breakage of the bubbles. On the other hand the froth should break down quickly after removal from the cell so as to allow of the ready collection of the floated mineral or concentrate in a condition suitable for feeding to vacuum filters, which remove sufficient water from the wet slimy concentrate to allow it to be transferred for sale or further treatment as may be required.

For this purpose " froth—stabilising reagents " may be necessary. These are distillation products of coal, wood or oil which are insoluble in water and with sufficient agitation are adsorbed to the air-water interfaces. The use of such reagents is out of date. In modern practice the amount of frother and the pulp density, *i.e.* ratio of crushed ore to water, are generally so controlled as to give adequately stable froth. It is much easier to do this in the alkaline circuits used with organic reagents now general in flotation practice than in the acid circuits used with oils in the early days of flotation.

The fourth necessary condition for successful flotation is that reagents be available to control the floatability of the different sulphides in the ore. These may be classed as " collectors " to collect the most readily floatable sulphides, the first to be separated and removed, " depressants " to keep the other sulphides present from floating by sinking or depressing them, and " activators " added to refloat or activate the depressed sulphides as and when required.

The fifth necessary condition for successful flotation is that the gangue or unwanted portion of the ore, the tailings, must remain unfloated, *i.e.* must be sufficiently wetted not to be held in the froth. Sometimes the depressant used for the sulphides also depresses the gangue, sometimes the gangue is sufficiently wetted during the operations involved, sometimes a " gangue modifying " or " wetting agent " must be added. Sodium silicate is widely used in alkaline circuits whilst sulphuric acid is cheap and effective in acid circuits.

The sixth necessary condition for successful flotation is that the acidity or alkalinity, the p_H value of the pulp must be adjusted to suit the flotation reagents used, natural acidity of the ore and salts such as aluminium sulphate and ferric sulphate occurring naturally in the ore may cause " toxic conditions " of the pulp, conditions causing destruction or non-adsorption of the flotation reagents. When necessary the hydrogen ion concentration is controlled and toxic conditions of the pulp are prevented by preliminary washing of the ore or by the addition of pulp conditioners, *i.e.* conditioning reagents such as lime, sodium carbonate and caustic soda.

The depressants used for a sulphide in a selective flotation circuit may also " condition " the pulp and depress or modify the gangue, thus, although six different conditions have been specified as necessary for successful flotation, and different reagents mentioned in connection with each, one reagent may perform more than one function and the operation of the process simplified accordingly. Thus it is quite usual to employ one reagent as frother, froth stabilizer and collector.

REAGENTS.

Although over two thousand reagents have actually been patented and many more have been suggested, less than a hundred are at all widely used in the flotation process by which more than 50,000,000 tons of ore are treated annually.

Pine oil and cresylic acid are the chief frothers, sulphuric acid, sodium silicate and the common alkalis are the chief gangue modifers and pulp conditioners. The common alkalis and a few simple metallic salts are used as depressants and activators.

Oils, once the most important and almost the sole class of collectors, have since 1930 been replaced by various organic compounds which yield suitable adsorbable anions on solution. From 1930 to 1940 development has been in the direction of using fewer and better purified reagents in smaller quantities. This has been made possible by the more accurate control of working conditions, particularly the hydrogen ion concentrations. Considerable developments are to be expected in the use of the newly introduced differential wetting agents which facilitate the differential flotation of non-metallic minerals, and also in the use of reagents with adsorbable polar cations.

The choice of reagents in a particular case must often be modified by the consideration of patent royalties, stability under local climatic conditions, regularity and purity of supply and, of course, cost. On the other hand an extremely expensive organic reagent suitable for some special purpose can sometimes be obtained at a very low price if required regularly in quantity.

Inorganic Reagents.

The inorganic reagents in general use are the common mineral acids and alkalis used for pulp conditioners and gangue modifiers.

Sulphuric acid is the most commonly used gangue modifier in acid circuits, but these are seldom employed now for ores unless much fine slime has to be dealt with. Acid circuits are sometimes used for the flotation of blende from a bulk concentrate or of fine depressed pyrites from an end-product.

Lime is used for pulp conditioning but also as a depressant for iron pyrites. Caustic soda counteracts previously added oils in differential flotation, depresses pyrites, helps sulphidising in the flotation of oxidised ores, may depress or float blende in different ores and assists in the emulsification of oils. Sodium carbonate and bicarbonate are used instead of lime with straight lead and zinc ores and with mixed sulphide ores if the sulphide content is high. They revive some pyrites.

Certain salts of the common metals are employed more particularly as depressants, activators and gangue modifying or wetting agents. Thus copper sulphate is used in differential flotation for activating depressed zinc blende, pyrites and pyrrhotite, it also accelerates the flotation of blende in zinc ores. Ferrous sulphate depresses pyrites in the presence of chalcopyrite.

The polysulphides and sodium sulphide are used as sulphidising reagents in the treatment of oxidised ores of lead and zinc. Sodium sulphide is also used to activate pyrites, to assist in the flotation of tarnished galena and blende and to act as a wetting agent with silicates and non-metallic minerals.

Potassium dichromate is used for depressing galena, activating marmatite, a double sulphide of iron and zinc, and for activating some copper minerals.

Sodium cyanide is used for depressing iron pyrites, as little as 1 part in a million parts of water may be effective. It is also used for this purpose in conjunction with lime for copper ores and, in conjunction with zinc sulphate, for depressing blende. It may be used alone for reconditioning blende. Sodium or potassium permanganate are occasionally used for mispickel (FeAsS).

Sodium phosphates are used as wetting agents, preferably the dihydrogen phosphate, and in the treatment of silicate ores and non-metallic minerals.

Sodium oleate is used for the flotation of malachite and certain non-metallic minerals.

Sodium silicate is the most widely used gangue modifier in alkaline circuits and has a deflocculating effect on gangue.

Sodium sulphite is used for depressing blende and pyrites, as is also sodium thiosulphate.

Hyposulphurous acid itself is used in Central Europe. "*Ehof*" a German reagent advertised for this purpose contains polythionates.

Zinc sulphate, often in conjunction with sodium cyanide, is widely used for depressing blende.

These salts are thought to act as depressants by supplying inorganic anions which prevent the collector being adsorbed by some minerals but not by others. Their utility has to be determined in practice by careful and systematic testing.

Organic Reagents.

These fall into three main classes: the frothers, the collectors and the differential wetting agents, the so-called "anodic reagents."

Frothers.—By far the most widely used frothers for sulphide ores are cresol, cresylic acid (*q.v.*), and pine oil. Pine oil is manufactured to various definite specifications for flotation purposes, it contains terpenes and camphors in various proportions. "*Flotol,*" manufactured in Germany, is a terpene alcohol obtained as a by-product in the manufacture of camphor.

Eucalyptus oil is also used as a frother generally when it can be obtained locally, it also has collecting properties.

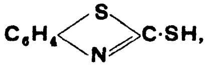
Free cresols are said to be present in "*Aerofloat 15,*" "*Aerofloat 25*" and "*Aerofloat 31.*" The reagents marketed by the largest and most influential manufacturers of flotation reagents in U.S.A. are now mostly sold under mystery numbers. This does much to frustrate scientific training and compels the practising metallurgist in flotation work to resort to the methods of the Dark Ages and employ "rule of catalogue numbers" for "rule of thumb." For oxidised ores and non-metallic minerals certain alcohols and alcohol derivatives, and compounds of the acids, are used.

The essential requirement for frothers appears to be the possession of a polar and a non-polar part, a part which repels water and a part which hydrates, such as has already been noted in cresol. The frothing properties of the alcohols increase with the length of the carbon chain up to about 7 or 8 carbon atoms but decrease thereafter. Generally speaking, in a homologous series the middle members are the best frothers, the higher members being less soluble. Sometimes this may be overcome by substituting the acid sulphate of the alcohol for the alcohol itself. The use of the many compounds which, according to these rules, can form good frothers, is restricted by the facts that many are not cheap enough and are not effective at sufficiently low concentrations.

Oleic acid, one of the earliest frothers used experimentally is now only employed commercially as a collector for certain non-sulphide minerals.

Collectors.—Of the organic reagents used as collectors the two main classes are the thio-derivatives of carbamide or of sodium carbonate and the thio-derivatives of cresylic or phosphoric acid.

Of the large class of mercapto compounds only one is used to any extent, namely, mercaptobenzthiazole,

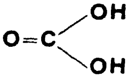


which is sold under the trade name "*Flotagen.*"

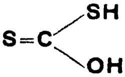
All these organic compounds, like those used as frothers, are heteropolar, their molecules possess a polar and a polar-non-polar part, but with this difference the polar part must have a specific affinity for the surface of a specific mineral whilst the polar part of the molecule of a frother need only have an affinity for water. The affinity for a sulphide surface seems to be connected with the possession of a sulphur atom with an unsaturated bond ($S=$). The adsorbed polar part of these collector molecules may be regarded as attached to the mineral surface with its water-repellant or air-avid end orientated outwards so that the surface presented to the air bubble is non-polar, one in which the atoms are co-valent. This hypothesis is supported by the experimental facts that the contact angle of different minerals (Fig. 2) is the same if they have been treated with the same collector and is the contact angle characteristic of the collector used; conversely the same mineral will give different contact angles when treated with different collectors, the contact angle in each case being that characteristic of the collector.

Examples of non-ionized collectors are known. At present, except for the *dixanthogens*, *e.g.* diethyl thioformate disulphide, their use for the collection of sulphides is highly restricted and their mode of action not yet understood.

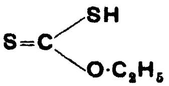
With orientated adsorption one would expect that the longer the carbon chain in the non-polar part of the polar-non-polar anion the more effective would be the collector, because the increased thickness of the non-polar part would mask the polar part of the coating. This is strikingly illustrated in the case of the xanthates. Xanthic acid is related to carbonic acid thus:



Carbonic acid, H_2CO_3.



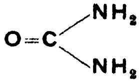
Thiol-thion carbonic acid.



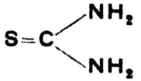
Xanthic acid.

Potassium xanthate may thus be also described as potassium ethyl dithiocarbonate. It is the most widely used and the cheapest of the xanthates. The substitution of the amyl, butyl or cetyl radicle gives us amyl, butyl and cetyl xanthates with increasing powers as collectors in certain cases, *e.g.* in the treatment of some gold ores.

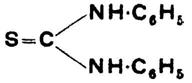
An older type of this class of collectors was thiocarbanilide which contains two phenyl groups instead of an alcohol radicle, thus:



Urea or carbamide.



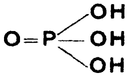
Thiocarbamide.

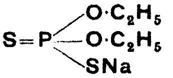


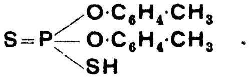
Thiocarbanilide.

This reagent is a weaker collector than the xanthates but it gives a better froth and, because it is slower in its action, is particularly useful in delicate differential work.

The "*Aerofloat*" group of reagents marketed mainly under 12 numbers are related to phosphoric acid, *e.g.* sodium diethyl dithiophosphate and dicresyl dithiophosphate:







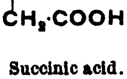
Some members of this group are both collectors and frothers, all are collectors.

The reagents mentioned have achieved great success with metallic sulphide ores, but have been of little commercial value for the differential flotation of non-metallic minerals and of oxidized ores. Oleic acid, fish-oil fatty acid and soaps of of these and other fatty acids and salts of the fatty acids, *e.g.* sodium lauryl sulphate and sodium lauryl phosphate, have given encouraging results as collectors using terpineol frother and other frothers.

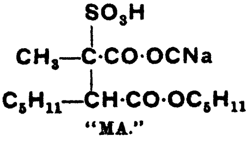
In 1938 a new type of reagent was investigated in which the cation instead of the anion was the polar non-polar part. One of these reagents, trimethyl cetyl ammonium bromide, $N(CH_3)_3(C_{16}H_{33})Br$, gave surprisingly satisfactory selective results on a laboratory scale. In 1940 a series of these reagents were put on the market under mystery numbers, one is said to be particularly useful for depressing graphite in the flotation of gold ores. Their mode of action is not clear, the compound mentioned above does not appear to dissociate in solution, others of this group appear to be differential wetting agents rather than collectors.

The "*Aerosol*" reagents are marketed definitely as wetting and deflocculating reagents and are described as the sodium salts of:

Dioctyl sulphosuccinic acid "OT."
Amyl methylamylsulphosuccinate "MA."
Diamylsulphosuccinic acid "AY."
*iso*Propyl naphthalenesulphonate "OS."



Succinic acid.

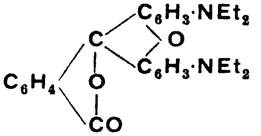


"MA."

These reagents are soluble in both polar and non-polar solvents. They are specially recommended as gangue depressants in the flotation of oxidized ores.

Although so much difficulty is met with in the treatment of most non-metallic minerals, coal is an exception. It can be floated very easily with light fuel oil, kerosene, or even coke oven liquor. Turpentine is a powerful collector and good frother for coal. Sodium cyanide is used to depress the contained iron pyrites. In the differential flotation of the coking and the non-coking constituents of a coal, tannin, starch, glue and also water-glass have been used as protective colloids. The low value of the fine product permits of the use of only the cheapest reagents for coal.

Certain rather unexpected reagents have been found of use in particular cases, *e.g.* Rhodamine B, an aminophenol derivative,



Rhodamine B.

for the depression of talc in some ores; quinaldine (2-methylquinoline, C_9H_6NMe) a nitrogen ring compound, a collector of copper pyrites and a depressor of blende in certain ores, but the total number of reagents at all widely used for flotation work is only two or three dozen.

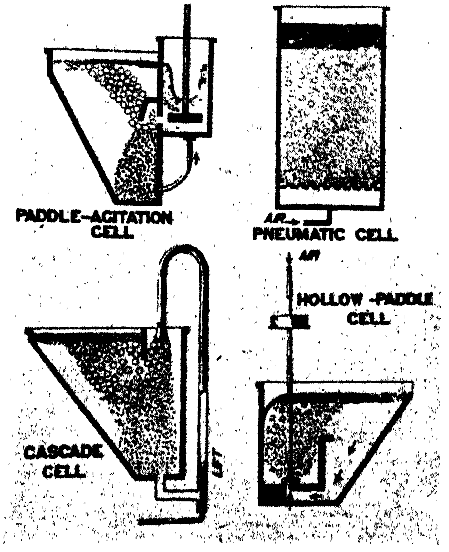


Fig. 3.

Flotation Machines.

A flotation machine should be continuous in operation, easy to start up after a temporary stoppage and free from periodical breakdowns It should also provide:

Adequate and adjustable aeration and agitation of the pulp (water and ground ore).
Adequate sub-division or emulsification and distribution (contact) of the reagents in the pulp.
Adequate but not excessive area for the collection and removal of the mineral-laden froth.

Any machine or appliance which fulfils these conditions is satisfactory, hence locally designed machines are often met with in practice. Three main types are favoured, namely: mechanical, pneumatic and cascade machines (Fig. 3).

Flotation Separation Tests.

In carrying out tests on ores it should always be borne in mind that, whatever apparatus and set procedure are employed, reliable results are not obtainable in *some* cases, except after systematic experimentation on a successively larger and larger scale. On the other hand with many ores the results obtained in small-scale tests can be duplicated in practice without any necessity for large-scale tests. Even in such cases the construction of a pilot plant should be regarded as a necessary preliminary to efficient mill design and operation.

The factors to be considered in carrying out flotation tests concern the character of the ore, the preparation of the ore for the test, and the conditions of the test itself thus:

Character of the Ore.

Presence of colloids or of primary slime.
Presence of soluble salts or of natural acidity.
Proportion of sulphides to gangue.
Degree of dissemination of the sulphides.
Relative hardness of gangue and the valuable minerals.
Components and chemical nature of the constituents of the gangue.
Flocculating properties of the gangue.
Relative floatability of the sulphides.

Preparation of the Ore.

History and reliability of the sample.
Kind of crushers.
Method of crushing.
Degree of comminution attained.

Conditions of the Test.

Nature and composition of the water used.
Proportion of water to ore.
Proper pulp conditioning.
Rate of feed and proportion of ore in circuit.
Method and degree of classification employed.
Addition of reagents before, during or after crushing.
Consistency of reagents and time of contact.
Chemical properties of the reagents used in relation to the nature of the circuit: acid, alkaline or neutral.
Amount of aeration and agitation, bubble size.
Duration of test.
Type of machine used.
Method of concentration, whether straight, bulk or selective.
Skill and experience of the operator.

Common Reagents Used for Tests.

Mineral Acids and Alkalis.

Sulphuric Acid.—(1) Gangue modifier in acid circuits; (2) with sodium sulphite to sink blende; (3) flotation of blende from a bulk concentrate; (4) flotation of lime-depressed pyrites; (5) used in sub-A machines if much fine slime.

Lime.—(1) Pulp conditioning; (2) neutralising acidity; (3) depressing iron pyrites.

Caustic Soda.—(1) Counteracts previously added oils; (2) depressant for pyrites; (3) helps sulphidising; (4) depresses or floats blende; (5) helps emulsification of oils.

Sodium Carbonate or Bicarbonate.—(1) Substitute for lime with straight lead and zinc ores; (2) carbonate used if the sulphide-content is high; (3) revives some pyrites.

Metallic Salts.

Copper Sulphate.—(1) Activating and reactivating blende; (2) activates pyrites to a less extent, also pyrrhotite.

Sodium Polysulphide.—For sulphidising oxidised ores.

Potassium Dichromate.—Activates copper ores and marmatite.

Potassium Permanganate.—For arsenical ores, etc.

Sodium Cyanide.—(1) In pine oil and xanthate circuits to depress blende and pyrites; (2) with lime for pyrites in copper ores; (3) for treating copper-activated blende.

Sodium Silicate.—Gangue modifier in neutral and alkaline circuits.

Sodium Sulphide.—(1) For tarnished galena and blende; (2) for activating pyrites and for sulphidising oxidised ores; (3) for wetting some minerals.

Sodium Sulphite and Thiosulphate.—For depressing blende and pyrites.

Trisodium Phosphate.—Wetting agent with oxidised ores and some copper ores.

Zinc Sulphate (use 3 parts $ZnSO_4,7H_2O$ or 2 parts $ZnSO_4,2H_2O$ for 1 part NaCN).—(1) Depresses blende, is sensitive, improved by sodium cyanide; (2) floats some blendes.

Simple Derivatives of Benzene.

Cresylic Acid.—Frother.

Orthotoluidine.—Frother and solvent.

Thio- and Phospho-Derivatives.

"Aerofloat," "Flotagen-S."

Derivatives of Carbanilide.

Thiocarbanilide, Potassium ethyl xanthate.

Distillation Products.

Pine Oil, Turpentine, Wood Tar, Coal Tar, Wood Tar Creosote.

Other Substances.

Eucalyptus Oil, Oleic Acid.

Conclusion.—The two essential rules in testing ores by flotation are:

- (i) All the test conditions kept as similar as possible to those which will prevail in practice.
- (ii) Exhaustive experimentation in attacking a difficult problem.

Amounts of Reagents Used.—The amounts required are generally within the limits given below:

Frothers	0·02–0·25 lb. per ton.
Collectors . . .	0·05–2·5 lb. per ton.
Depressants . . .	0·05–1·0 lb. per ton.
Activators . . .	0·01–2·0 lb. per ton.

B. W. H.

FLUAVIL. A yellow amorphous resin soluble in cold alcohol found in gutta (*v.* Vol. III, 30*b*).

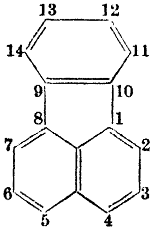
"FLUID GELATIN." Aluminium salts of higher fatty acids (*v.* Aluminium, Vol. I, 293*d*).

FLUOCERITE. Fluoride of cerium (40%), lanthanum (30%), and yttrium (3%) earths, crystallised in the hexagonal system. It is reddish-yellow with resinous lustre, and massive, rarely as crystals. Sp.gr. 5·70, 5·93. It occurs in pegmatite veins with gadolinite, orthite, etc., at Osterby, Finbo and Broddbo in Sweden (P. Geijer, Geol. För. Förh. Stockholm, 1921, **43**, 19).

L. J. S.

FLUOCOLLOPHANITE *v.* Collophanite (Vol. III, 294*a*).

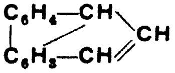
FLUORANTHENE (1:8 - Benzacenaphthene; *idryl*), $C_{16}H_{10}$,



was discovered independently by Fittig and Gebhard (Ber. 1877, **10**, 2143; Ann. 1878, **193**, 142) in coal tar, and by Goldschmiedt in "stupp," a mixture of hydrocarbons obtained in distilling mercury ores at Idria (Ber. 1877, **10**, 2022). It is obtained from the fraction of coal tar boiling higher than anthracene, by redistilling it at 250°/60 mm. A mixture passes over of pyrene and fluoranthene, which may be separated by repeated crystallisation of their picrates from alcohol; *fluoranthene picrate* separates in orange needles, m.p. 184–185°. Fluoranthene has been isolated from the higher boiling fractions of "acetylene tar," produced by leading acetylene, mixed with hydrogen, through a porcelain tube at 640–650°C. (Meyer and Taeger, *ibid.* 1920, **53** [B], 1264); it is also found, together with other polycylic aromatic hydrocarbons, among the products of the reductive fission of bituminous- and lignin-containing substances (I.G. Farbenind. A.-G., B.P. 435254; F.P. 781543; Chem. Zentr. 1936, II, 3618).

The hydrocarbon crystallises from alcohol in needles or monoclinic plates, melting at 110°. It has b.p. 250–251°/60 mm., 217°/30 mm. It is sparingly soluble in cold, readily soluble in boiling alcohol; soluble in ether, chloroform, carbon disulphide, benzene and glacial acetic acid. Warm concentrated sulphuric acid dissolves the hydrocarbon, giving a deep blue colour.

The discoverers of fluoranthene erroneously ascribed to it the formula $C_{15}H_{10}$, and the constitution



The true constitution was established by synthesis from β-9-fluorenyl-propionic acid, which was cyclised to 4-keto-1:2:3:4-tetrahydrofluoranthene. This was reduced to tetrahydrofluoranthene, which yielded fluoranthene on distillation in carbon dioxide over red-hot litharge on pumice (von Braun, Anton and Wagner, Ber. 1929, **62** [B], 145).

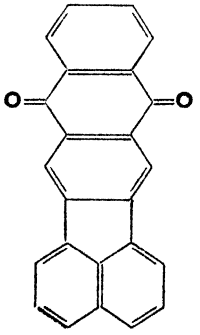
Reduction with sodium and amyl alcohol, or with hydrogen and a nickel catalyst in decalin under pressure at 230°, gives tetrahydrofluoranthene, $C_{16}H_{14}$, m.p. 74–75°, b.p. 203–205°/2 mm.; decahydrofluoranthene, $C_{16}H_{20}$, b.p. 181–183°/12 mm. and perhydrofluoranthrene, $C_{16}H_{26}$, b.p. 168–170°/12 mm. (von Braun and Manz, *ibid.* 1930, **63** [B], 2608).

Oxidation with chromic acid yields *fluoranthenequinone* (3:4), m.p. 180°, and by further oxidation *fluorenone*-1-*carboxylic acid*, m.p. 192°. The latter is converted by heating with lime to *fluorenone*, and by fusion with caustic potash to iso*diphenic* acid (diphenyl-2:3′-dicarboxylic acid).

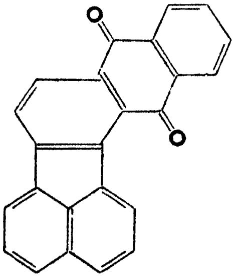
Nitration of the hydrocarbon with fuming nitric acid yields a trinitroderivative; on nitration in glacial acetic acid there is formed, in *ca.* 20% yield (purification being wasteful), 4-nitrofluoranthene, m.p. 159–160°. This may be reduced to the amine, which is easily diazotised. The diazonium compound couples with β-naphthol to give a deep red azo-dye.

Sulphonation and bromination, under controlled conditions, yield similarly the 4-monoderivatives (von Braun and Manz, Annalen, 1931, **488**, 111; von Braun and Anton, Ber. 1934, **67** [B], 1051).

On the other hand, acylation by the Friedel-Crafts method leads to derivatives with the substituent groups mainly in the 12-position, and in the 4-position in the by-products. Thus with phthalic anhydride and aluminium chloride in carbon disulphide, fluoranthene yields 12-*o*-carboxybenzoylfluoranthene, m.p. 212°. The acid chloride of this, heated in trichlorobenzene, cyclises to the quinones (I), m.p. 228°, red, giving a violet vat, and (II), m.p. 332°, yellow, giving a blue vat (von Braun, Manz and Kratz, Annalen, 1932, **496**, 170).



I.

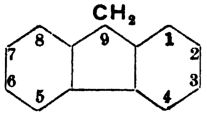


II.

Fluoranthene and its derivatives have been suggested as intermediates for dyestuffs. Its amino derivatives may be condensed with 1:4-quinones to give pigment dyes, or intermediates of oxazine or sulphur dyestuffs (I.G. Farbenind. A.-G., B.P. 408456; Amer. Chem. Abstr. 1934, **28**, 5678; *see also* I.G. Farbenind. A.-G., G.P. 575953; Amer. Chem. Abstr. 1933, **27**, 4819; G.P. 595024; Amer. Chem. Abstr. 1934, **28**, 4069).

FLUORANTHENEQUINONE *v.* FLUORANTHENE.

FLUORENE. o-*Diphenylenemethane*,



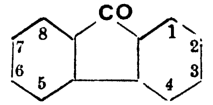
was discovered by Berthelot in coal tar (Compt.) rend. 1867, **65**, 465; Ann. Chim. Phys. 1867, [iv], **12**, 222). Obtained (1) by passing the vapour of diphenylmethane through a red-hot tube (Graebe, Annalen, 1874, **174**, 194; Ber. 1874, **7**, 1624), (2) by heating diphenylmethane or di*cyclo*hexylmethane with Pt-charcoal at 300° (Zelinski, Titz and Gaverdovskaja, *ibid.* 1926, **59** [B], 2590), (3) by reduction of fluorenone by heating either with zinc dust (Fittig, *ibid.* 1873, **6**, 187) or with hydriodic acid and red phosphorus to 150–160° (Graebe, *ibid.* 1874, **7**, 1625), (4) by diazotising 2-amino-diphenylmethane and heating the aqueous solution of the diazonium salt so obtained (Fischer and Schmidt, *ibid.* 1894, **28**, 2787), (5) by heating the quinoline salt of fluorene-9-carboxylic acid to 160–170° (Staudinger, *ibid.* 1906, **39**, 3067, Note 1) or the free acid to 290° (Delacre, Bull. Soc. chim. 1902, [iii], **27**, 877): the *fluorene*-9-*carboxylic acid* may be prepared by condensing ethyl trichloroacetate with benzene in the presence of aluminium chloride (Delacre, *l.c.*). The high-boiling fractions of tar oil, after depositing naphthalene and anthracene, are distilled; the fraction boiling between 295° and 310° contains the greater portion of the fluorene, which, on fusion with caustic potash at 280°, is converted into a solid potassium compound (Weissgerber, Ber. 1901, **34**, 1659), this was originally separated mechanically from the fused hydrocarbons and the fluorene regenerated by treatment with water (G.P. 124150). The sodium compound, also used in the separation, is obtained by fusing the mixture of hydrocarbons with sodium or sodamide at 110–250° (G.P. 203312). In the presence of aniline or other organic bases, the reaction proceeds more smoothly and at a lower temperature (G.P. 209432). Recrystallisation from alcohol and glacial acetic acid and precipitation of the picric acid compound (m.p. 81°), may be used in the purification. Lustrous laminæ, m.p. 116°, b.p. 294–295°. Sparingly soluble in cold, readily in hot alcohol; readily soluble in ether, benzene and carbon disulphide.

Isomeric diphenylenemethanes were described by Carnelley (J.C.S. 1880, **37**, 708), who obtained them by passing the mixed vapours of benzene and toluene through a red-hot tube. Stereoisomerism in 9-amino derivatives of fluorene had been described by Kuhn and Jacob (Ber. 1925, **58** [B], 1432) and by Schlenk and Bergmann (Annalen, 1928, **463**, 1, 98; **464**, 1; Ber. 1929, **62** [B], 745), but has not been confirmed by Kliegl and his collaborators (Ber. 1926, **59** [B], 631; 1929, **62** [B], 1327; 1930, **63** [B], 1262). Measurements of the dipole moment of 2:7-dinitrofluorene (4·80 D units) indicate, however, that fluorene in solution exists as a flat molecule (Hughes *et al.*, Chem. and Ind. 1936, **55**, 545).

The negative character of the methylene group, as shown by the formation of derivatives with sodium and potassium (*v. supra*) and lithium (by the action of lithium ethyl) resembles closely that found in *cyclo*pentadiene. The decomposition of Grignard compounds by fluorene with the formation of fluorenyl magnesium halide and a paraffin hydrocarbon, condensation reactions with aldehydes, esters (Thiele, Ber. 1900, **33**, 85; Wislicenus, *ibid.* 1900, **33**, 771) and with nitrobenzene (Hailwood and Robinson, J.C.S. 1932, 1292), emphasise this characteristic. A number of reactions have been described involving the conversion of substances having a phenanthrene skeleton to derivatives of fluorene and *vice versa, e.g.* alkaline fusion of phenanthrenequinone yields 9 - oxyfluorene - 9 - carboxylic acid (Schmidt and Bauer, Ber. 1905, **38**, 3738) while phenanthrene is obtained during the pyrolysis of methylfluorene (Graebe, *ibid.* 1904, **37**, 4145). Oxidation with chromic acid yields fluorenone (*q.v.*); with potassium permanganate, *o*-phthalic acid; with fused caustic potash, *o*-phenylbenzoic acid; while heating with sulphur or distillation over heated lead oxide yields bisdiphenylene-ethane and bisdiphenylene-ethylene (red needles, m.p. 188°). Vapour phase oxidation with air in the presence of steam at 300–500° over vanadium pentoxide as catalyst gives rise to *fluorenone* (U.S.P. 1892768). Reduction with hydriodic acid and red phosphorus yields a *decahydrofluorene*, $C_{13}H_{20}$ (Schmidt, Ber. 1907, **40**, 4566; 1908, **41**, 4228); *dodecahydrofluorene*, $C_{13}H_{22}$, was described by Spiegel (*ibid.* 1908, **41**, 885; 1909, **42**, 919). The decahydride and dodecahydride are obtained together on heating fluorene with hydrogen in the presence of nickel oxide below 290° and 120 atm. (Ipatiev, *ibid.* 1909, **42**, 2093). Hydrogenation at 300° and 153 atm. over oxides of cerium and osmium gives 93% dodecahydrofluorene; with nickel oxide action is slower and decahydrofluorene is formed (Sadikov and Michailov, *ibid.* 1928, **61** [B], 1792). With nitric acid (sp.gr. 1·4) in glacial acetic acid, 2-*nitrofluorene* (needles from 50% acetic acid, m.p. 156°) is formed (Diels, *ibid.* 1901, **34**, 1759; Kuhn, Organic Syntheses, 1933, XIII, 74). Fuming nitric acid in glacial acetic acid solution gives 2:7-*dinitrofluorene* (m.p. 334°) and also the 2:5-derivative, (m.p. 207°) separable by crystallisation from acetic acid (Morgan and Thomason, J.C.S. 1926, 2691; Courtot, Ann. Chim. Phys. 1930, [x], **14**, 5). Nitration of 9-substituted derivatives proceeds similarly, but frequently oxidation occurs simultaneously with the formation of substituted fluorenones (Anantakrishnan and Hughes, J.C.S. 1935, 1607; Langecker, J. pr. Chem. 1931, [ii], **132**, 145; Huntress and Cliff, J. Amer. Chem. Soc. 1932, **54**, 826). 3-*Nitrofluorene* has been obtained from 3-nitro-2-aminofluorene by treatment of the derived diazonium salt with cuprous oxide (Bardout, Anal. Asoc. Quim. Argentina, 1931, **19** 117). Sulphuric acid in acetic anhydride solution (Wedekind and Stüsser, Ber. 1923, **56**, [B], 1561) or chlorsulphonic acid gives *fluorene*-2-*sulphonic acid* (m.p. 154·5°); further sulphonation gives the 2:7-*disulphonic acid* (Courtot and Geoffroy, Compt. rend. 1924, **178**, 2259; Schmidt, Retzlaff and Haid, Annalen, 1912, **390**, 217). Chlorination in chloroform solution at 0° gives the 2-*chloro*- (m.p. 142°) and 2:7-*dichloro*- (m.p. 154–155°) *derivatives*. These are difficult to separate but oxidation of the mixed chloro-compounds with sodium dichromate in acetic acid yields a separable mixture of the corresponding chloro-fluorenones. According to Buffle (Helv. Chim. Acta, 1932, **15**, 1483), 2-chlorofluorene is best prepared in benzene or acetic acid solution at 80–90° in the presence of iodine. Bromination in chloroform gives 2-*bromofluorene* (m.p. 110°), difficult to separate from the accompanying dibromo-derivative (Courtot and Vignati, Bull. Soc. chim. 1927, [iv], **41**, 58). At 113–115°, 2 mol. of bromine yield 2:7-*dibromofluorene*, m.p. 166–167° (Graebe and von Mantz, Annalen, 1896, **290**, 239). 2-Chlorofluorene and 2-bromofluorene have been obtained from 2-aminofluorene by the Sandmeyer reaction. 9-*Chloro*- (m.p. 92°) and 9-*bromo-fluorene* (m.p. 104°) are prepared from 9-fluorenol by the action of phosphorus halides. 2-*Iodofluorene* was prepared in 30% yield from 2-diazonium fluorene and KI solution (Chanussot, Bull. Soc. chim. 1927, [iv], **41**, 1626), and also from fluorenylhydrazine hydrochloride and aqueous KI and iodine (Korczyński, Karlowska and Kierzek, *ibid.* 1927, **41**, 65). 2-*Fluorofluorene* (m.p. 100°) was prepared from the 2-diazonium fluoborate (Bergmann, Hoffmann and Winter, Ber. 1933, **66** [B], 46). The Friedel and Crafts reaction with acid chlorides gives mono- and di-acyl and aroyl derivatives which are convenient intermediates for the preparation of amines (by Beckmann rearrangement of the oximes) and carboxylic acids (oxidation with chromic acid), substitution occurring first in the 2-position and then in the 7-position (Dziewoński *et al.*, Bull. Acad. Polonaise, 1932, **A**, 109, 293; Rocz. Chem. 1932, **12**, 167; 1933, **13**, 291; in French).

Reduction of nitro-compounds with Zn or Sn and Hd yields the corresponding amines. 2-Nitrofluorene on mild reduction with zinc and alcohol containing calcium chloride gives 2:2′-*azoxybisfluorene* (m.p. 279° decomp.), which on further reduction with zinc and acetic acid in phenol yields 2 (or 2′)-*amino*-1:2′ (or 2:3′)-*difluorylamine* (Cislak, Eastman and Senior, J. Amer. Chem. Soc. 1927, **49**, 2318). 2:7-*Diaminofluorene*, m.p. 164°, has been suggested as a reagent for the detection of Zn, Cd and Cu (Schmidt and Hinderer, Ber. 1931, **64** [B], 1793), nitrate ions (Eitel, Z. anal. Chem. 1934, **98**, 227) and blood, and has been used in the preparation of azo-dyes. The following carboxylic acids have been obtained by normal methods: 1-, m.p. 245–246°, *ethyl ester*, m.p. 53·5° (Fittig and Liepmann, Annalen, 1880, **200**, 15), 2-, yellow crystals subliming at 340°, *methyl ester*, m.p. 120° (Fortner, Monatsh. 1904, **25**, 448); 4-, m.p. 175°, *methyl ester*, m.p. 64° (Graebe and Aubin, Annalen, 1888, **247**, 283). Fluorene forms many addition compounds, *e.g.* with picric acid, m.p. 81°; with 1:3:5-trinitrobenzene, m.p. 105°; with 2:4:6-trinitrotoluene, m.p. 85°.

FLUORENONE,



This cyclic ketone was discovered by A. Schmitz who heated diphenic acid with its own weight of quicklime (Annalen, 1878, **193**, 117; *cf.* Fittig and Ostermayer, Annalen, 1873, **166**, 376; Kerp, Ber. 1896, **29**, 228). It is also formed by the oxidation of fluorene with chromic acid. Graebe and Rateanu (Annalen, 1894, **279**, 258) used sodium dichromate and acetic acid; Fanto recommended the addition of sulphuric acid (Monatsh. 1898, **19**, 584; *cf.* J. Schmidt and B. Wagner, Ber. 1910, **43**, 1797). It may be obtained in almost quantitative yields by heating diphenic acid or anhydride or fluorenone-4-carboxylic acid at 360° (Huntress, Hershberg and Clipp, J. Amer. Chem. Soc. 1931, **53**, 2720; Huntress and Cliff, *ibid.* 1933, **55**, 2559).

The diethyl acetal, 9:9-diethoxyfluorene from the corresponding dichloro-compound and alcoholic potash, is hydrolysed to fluorenone by acids (Smedley, J.C.S. 1905, **87**, 1252).

Fluorenone separates as yellow crystals from alcohol, m.p. 83·5–84°, b.p. 341·5°/760, it is slowly volatile in steam, insoluble in water and easily soluble in alcohol and ether. The solution in concentrated sulphuric acid is bright violet (Wislicenus and Waldmüller, Ber. 1908, **41**, 3339, other authors say deep reddish-violet or purple-red), it is basic to strong acids (Stobbe and Seydel, Annalen, 1909, **370**, 135), and the nitrate, perchlorate and addition products with metallic salts are known.

Fluorenone can be destructively oxidised by chromic acid mixture, alkaline permanganate oxidises it very slowly to phthalic acid. Distillation with zinc dust gives fluorene; it is reduced to fluorenyl alcohol by sodium amalgam (Barbier, Ann. Chim. Phys. 1876, [v], **7**, 504); by zinc in glacial acetic acid (Kerp, Ber. 1896, **29**, 230); by zinc dust in alcoholic potash or ammonia (Werner and Grob, Ber. 1904, **37**, 2895); by aluminium amalgam in 80% alcohol (Cohen, Rec. trav. chim. 1919, **38**, 119); and by aluminium *iso*propoxide (Lund, Ber. 1937, **70** [B], 1520). With zinc dust and acetyl chloride in ethereal solution, $\alpha\beta$-bis-diphenylenethylene, $\alpha\beta$-diacetoxy-bis-diphenylenethane (tetraphenylenepinacone diacetate) and, as chief product, tetraphenylenepinacolin are produced (Klinger and Lonnes, Ber. 1896, **29**, 2154).

Since phenanthrenequinone (and its derivatives) are converted into 9-hydroxyfluorene-9-carboxylic acid (and its derivatives) by warming with caustic potash solution (Baeyer, Ber. 1877, **10**, 125, Anschütz and Schultz, Annalen, 1879, **196**, 50, and others), and the acids lose carbon dioxide and undergo oxidation on boiling with water in presence of air, substitution derivatives of fluorenone can be thus prepared (J. Schmidt and K. Bauer, Ber. 1905, **38**, 3738; *cf.* Huntress and Cliff, *l.c.*; Mascarelli, Gazzetta, 1936, **66**, 843).

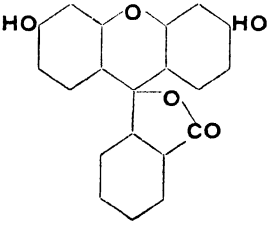
Derivatives of fluorenone may also be obtained by diazotisation of substituted *o*-aminobenzophenones and subsequent boiling. 3-*Methoxyfluorenone*, m.p. 99°, is produced in good yield by this method (F. Ullmann and H. Bleier, Ber. 1902, **35**, 4278).

With bromine or nitric acid, substituent groups enter the 2–, 7– and 3– positions in succession (Schmidt and Bauer, *l.c.*, 3760). 1:8-*Dinitrofluorenone* can be obtained starting with 9-acetaminofluorene whilst other substitution products can be made from the corresponding phenanthrenequinone derivatives.

Fluorenone-oxime, $[C_6H_4]_2\cdot C{:}NOH$, m.p. 195°, is obtained from fluorenone and hydroxylamine (Spiegler, Monatsh. 1884, **5**, 195; J. Schmidt and J. Söll, Ber. 1907, **40**, 4258). Its potassium salt results from the action of amyl or ethyl nitrite on fluorene in presence of ethereal-alcoholic potassium hydroxide (Wislicenus and Waldmüller, Ber. 1908, **41**, 3335). The potassium salt of *aci*-9-nitrofluorene results when ethyl nitrate is employed. Reduction of the oxime gives the *imine* (Kliegl, Ber. 1910, **43**, 2494).

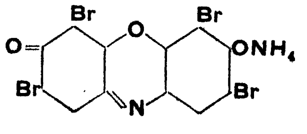
J. T. H.

FLUORESCEIN,



the dyestuff obtained by condensing phthalic anhydride with resorcinol (Baeyer, Ber. 1871, **4**, 558; *cf.* U.S.P. 1931049) preferably in presence of a condensing agent such as zinc chloride. It is of little value as a textile dye-stuff as dyeings on silk and wool are very fugitive; its highly fluorescent sodium salt is however marketed as *Uranine*. More important are its halogenated derivatives, particularly the eosines and erythrosines; some of these, such as dichlorofluorescein, find application as adsorption indicators (Kolthoff, Lauer and Sunde, J. Amer. Chem. Soc. 1929, **51**, 3273; Bambach and Rider, Ind. Eng. Chem. [Anal.], 1935, **7**, 165). Its formation is used as a test for resorcinol and for phthalic acid, its fluorescence being still visible at a dilution of 1:40 million.

FLUORESCENT BLUE. Iris Blue, the ammonium salt of tetrabromo-hydroxy-diphenoxazone,



FLUORINE. Sym. **F**. At. wt. 19·00. Ampère, in 1810, first pointed out the analogy between hydrochloric acid and the gas evolved from a mixture of fluorspar and sulphuric acid; he assumed the existence of an element similar to chlorine, and further that the acid obtained from fluorspar was a hydrogen compound. Berzelius and Davy, a few years later, more fully established this view.

The name fluorine was given to the supposed element on account of its being a constituent of fluorspar. Many attempts were made to isolate the element, but they failed, largely because of the great affinity of fluorine for other elements. It was not until 1886 that Moissan developed a satisfactory electrolytic method of preparation (*vide infra*).

Occurrence.—Fluorine occurs almost exclusively in the combined state. Very small amounts of the free element have, however, been detected in certain specimens of fluorspar. The chief fluorine minerals are calcium fluoride, CaF_2 *fluorite* or *fluor-spar* (*q.v.*) and sodium aluminium fluoride, $3NaF, AlF_3$ *cryolite* (*q.v.*), which are the main raw materials for the preparation of fluorine and its compounds.

Combined fluorine is found in many other minerals, among which the apatites and phosphorites are of special note. Its presence in conjunction with silica in phosphate minerals used in the preparation of superphosphate gives rise to silicon tetrafluoride, which must be eliminated by special methods (Sisco, Trans. Electrochem. Soc. 1924, **46**, 16). River and spring water may contain dissolved fluorides, varying in amount from a fraction of a milligram to 6 mg. per litre. Fluorine compounds have also been detected in volcanic gases. In the animal kingdom combined fluorine occurs as a normal constituent of the enamel of teeth, in bone, and in marine shells, while it has been shown to be present in the tissues in association with phosphorus. It is also found in varying small amounts in the vegetable kingdom, *e.g.* in certain grasses, in fossil woods, in grapes, and in malt extract. It is apparently of great importance in the animal economy and is also essential for the development of certain plants.

Isolation of Fluorine.—Attempts to isolate elementary fluorine which were made prior to Moissan's successful application of the electrolytic method in 1886 included the decomposition of metallic fluorides (*e.g.* CeF_4,H_2O or PbF_4) by heat, the decomposition of metallic fluorides (*e.g.* AgF) by other halogens, and the action of oxidising agents on fluorine compounds. Some at least of these early attempts met with failure only on account of the special difficulties inherent in the isolation of the new element.

The isolation of fluorine was achieved for the first time by Moissan (Compt. rend. 1886, **102,** 1543). It had been known since the time of Faraday that anhydrous hydrofluoric acid was a bad conductor of the electric current. Moissan discovered that it became conducting when it contained a small quantity of potassium hydrogen fluoride, KF,HF, and it was the electrolysis of the resulting solution which first yielded the element in the free state. The apparatus employed consisted of a platinum-iridium U-tube 9·5 cm. high and 1·5 cm. diameter (Fig. 1), each limb of which was provided with a hollow cylinder screwed into it. These cylinders were closed by fluorspar plugs (F) through which the electrodes passed. The cathode was of platinum and the anode of an alloy of platinum with 10% of iridium. In the early experiments this apparatus was cooled in a bath of boiling methyl chloride (−23°), but in later work a mixture of acetone and carbon dioxide snow was used. Hydrogen was evolved at the cathode and fluorine at the anode, the rate of gas evolution being 1·5–2·0 litre per hour. Attack of the electrodes was considerable, the loss being about 1 g. of electrode material per ampere-hour. In 1899 Moissan improved his apparatus by substituting a copper U-tube for that of platinum. This contained 200 c.c. of anhydrous hydrogen fluoride and 50 g. of the acid fluoride. A current of 15–20 amperes at 50 volts was used. Anhydrous hydrogen fluoride was prepared by treating a known volume of commercial hydrofluoric acid with sufficient potassium carbonate to neutralise about a fourth part, the mixture being then distilled in a leaden retort heated in an oil-bath at 120°. This distillation eliminates silica, which remains in the residue as potassium fluosilicate. The distillate was converted to the acid fluoride, KF,HF, by partial neutralisation with potassium carbonate. This salt was dried completely, first on a water bath at 100° and then over fused potash in vacuum. The dried salt was then distilled in a copper vessel, the first portions of distillate being rejected as containing traces of water. A copper, silver or platinum receiver may be used. The anhydrous acid boils at 19·5°.

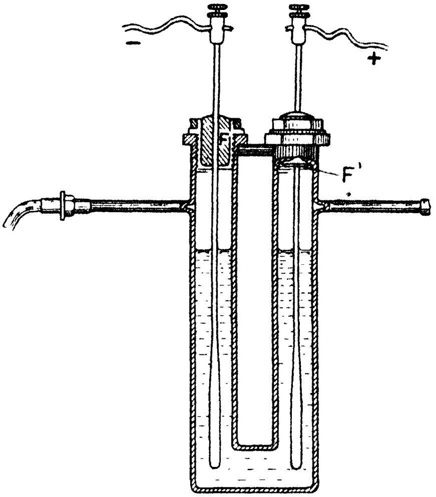


Fig. 1.

Moissan also electrolysed the double fluoride itself, which fuses to a colourless liquid. The experiment was done, as before, in a U-tube of platinum, but the latter was strongly attacked. Modern methods of preparing fluorine are based on this experiment, the electrolytes most commonly employed being either molten potassium hydrogen fluoride (m.p. 227°) or the molten compound $KF,3HF$ (m.p. 65°).

Various cells have been developed in recent years for the laboratory preparation of fluorine. Moissan's experiments with $KF,3HF$ were followed up by Lebeau and Damiens (Compt.) rend. 1925, **181**, 917), who employed a nickel anode and a cathode of either nickel or copper. Their method, modified in detail, is described by Cady and Henne in a recent publication (Inorganic Syntheses, Vol. I. Editor-in-Chief: H. S. Booth. McGraw-Hill Publishing Company, Ltd. 1939). The electrolyte is contained in a cylindrical pot of "*Monel*" metal or steel, which serves as the cathode. The anode is a co-axial cylinder of nickel, supported inside a cylindrical copper diaphragm. The electrolyte is prepared by the addition of anhydrous hydrogen fluoride, which may be obtained in some localities as a technical product, to the acid fluoride KF,HF. The optimum operating temperature is 73–75°.

E. I. Du Pont de Nemours and Co. (B.P. 425979) have described a cell for the production of fluorine by the electrolysis of a nearly saturated solution of KF,HF in anhydrous hydrogen fluoride. The cell is constructed of an alloy steel, and a nickel anode is supported inside a perforated steel cylinder. Fredenhagen and Krefft (Z. Elektrochem. 1929, **35**, 670) recommend the use of an electrolyte with 1·8 g. molecule of hydrogen fluoride per gram-molecule of potassium fluoride. In a cell described by Mathers and Stroup (Trans. Electrochem. Soc. 1934, **66**, 113) the electrolyte is the acid fluoride of caesium, $CsF,2HF$, which melts at 19°, the cell being constructed of magnesium.

Ruff and Ascher (Z. anorg. Chem. 1929, **183**, 193) have drawn attention to the possible use of cobaltic fluoride, CoF_3, as a source of fluorine. This substance, which must be produced from cobalt or cobaltous fluoride and fluorine, evolves fluorine when heated and might be found to afford a ready means of generating small amounts of the gas as required.

Electrolysis of the acid fluoride KF,HF in the molten state has been described by a number of authors. Argo, Mathers, Humiston and Anderson (J. physical Chem. 1919, **23**, 348) have used an apparatus constructed of copper, with a carbon anode surrounded by a perforated copper diaphragm. The electrolyte (KF,HF) is maintained in the molten condition at 225–250° by an external winding of resistance wire. Meyer and Sandow (Ber. 1921, **54** [B], 759) have developed this apparatus further, and make use of a pot of Acheson graphite as a container for the molten electrolyte. This also serves as a cathode, the anode being constructed, as before, of carbon. Fredenhagen (Chem. Ind. 1929, **22**, 197; G.P. 493873, 1928) also used the acid fluoride KF,HF as electrolyte, together with a graphite anode. The molten electrolyte may be held in an electrically heated pot of silver or copper, which served as the cathode. Jones (J. physical Chem. 1929, **33**, 801) employed a vessel of magnesium, together with a carbon anode, while Schumb and Gamble (J. Amer. Chem. Soc. 1930, **52**, 4302) used monel metal for the outer pot. In an apparatus described by Denbigh and Whytlaw-Gray copper was used (J.S.C.I. 1934, **53**, 139T). Dennis, Veeder and Rochow (J. Amer. Chem. Soc. 1931, **53**, 3263) devised a V-shaped cell, constructed of heavy copper tubes, brazed at the junction, and carrying graphite electrodes held in bakelite plugs. Miller and Bigelow (J. Amer. Chem. Soc. 1936, **58**, 1585) use a nickel U-tube as a container for the molten acid fluoride. This type of cell was used in studies on the fluorination of organic compounds. In a cell described by Bodenstein (Chem. Fabr. 1935, **8**, 283) the constructional material is electron metal with welded joints. The anode is of graphite and the cathode of silver. Electrolysis is carried out at 250°, and the electrodes are inserted through the bottom of the cell.

There is little indication in the literature of the relative merits of the above cells. In all of them the use of carbon anodes leads to contamination of the fluorine by carbon fluorides. Swelling of the carbon anodes as a result of the formation of the interstitial compound, carbon monofluoride, is a further source of difficulty. It is also essential to operate with anhydrous materials. Booth (*op. cit.* Vol. I, p. 137) states that the high temperature method, using KF,HF as electrolyte, is to be recommended for ordinary laboratory purposes and for intermittent use. Full details for the construction and operation of a high-temperature copper cell are given by Booth (*op. cit.*). A fluorinated rubber preparation for producing a film which protects metal parts against fluorine has been described recently (I.G. Farbenind., G.P. 642883).

Purification of Fluorine.—Fluorine as obtained in Moissan's apparatus contains small quantities of hydrogen fluoride, which may be removed by passage through a copper tube cooled to −80°, and then through two tubes packed with sodium fluoride, which is converted into the acid salt. It is essential to operate with an electrolyte which is anhydrous, as otherwise the gas evolved always contains the oxide F_2O. When fluorine is prepared with carbon anodes the gas evolved may contain carbon fluorides, as well as ozone, oxygen and fluorine oxide, which can be separated only by a tedious process of fractionation. For many purposes such, for example, as the direct fluorination of organic compounds, purification of fluorine is not necessary. In determining physical properties of the element, however, it is essential. Passage of the gas through a tube cooled in a bath of liquid air rich in oxygen removes impurities other than oxygen, fluorine oxide and a trace of carbon tetrafluoride. The first two of these impurities arise from the presence of moisture in the electrolyte or apparatus and are normally removed by operating the cell for a considerable period (Cady and Hildebrand, J. Amer. Chem. Soc. 1930, **52**, 3839; *see also* Aoyama and Kanda, Bull. Chem. Soc. Japan, 1937, **12**, 409, 455, 458, 463, 469, 473, 511, 522. The series of publications by the last-mentioned authors gives considerable information on the manipulation of fluorine).

Atomic Weight of Fluorine.—The atomic weight of fluorine was determined by Davy over seventy years before Moissan isolated the element, his method consisting of the transformation of calcium fluoride to calcium sulphate. The values obtained varied from 18·82 to 19·03. Other early determinations were made among others by Berzelius, Dumas and Moissan. Aston's mass spectrographic measurements showed that the element had no isotopes, and gave an atomic weight of 19·00 (Phil. Mag. 1920, **40**, 628). Moles and his co-workers have carried out a series of precise determinations of the density of methyl fluoride, the most recent of which gave an atomic weight of 18·998 (Gazzetta, 1926, **56**, 915). Smith and van Haagen (Carnegie Inst. Washington, Publ. No. 267, 1918) found a value of 19·002, based on the ratios $2NaF/Na_2B_4O_7$ and Na_2SO_4/NaF, while McAdam and Smith found the value 19·0133 from a study of the conversion of $NaCl$ to NaF (J. Amer. Chem. Soc. 1912, **34**, 592). Determinations of the density of methyl fluoride by means of the buoyancy balance have given the value 18·996 (Cawood and Patterson, Phil. Trans. 1936, A, **236**, 77). Moles and Toral (Z. anorg. Chem. 1938, **236**, 225) measured the density of silicon tetrafluoride and, taking the atomic weight of silicon as 28·104, found that of fluorine to be 18·995±0·001.

Physical Properties.—Gaseous fluorine has a pale-yellow colour. Its absorption spectrum in the visible and near ultra-violet regions is continuous in character and shows a maximum absorption at about 2,800A. The index of refraction (λ5890A) is 1·00195. Brockway (J. Amer. Chem. Soc. 1938, **60**, 1348) determined the internuclear distance in the fluorine molecule by means of electron diffraction measurements as 1·45±0·05A, a value which is 14% greater than that to be expected for a normal single covalent linkage. The molecular diameter, derived from viscosity measurements with the gas, is 3·02A (Kanda, Bull. Chem. Soc. Japan, 1937, **12**, 463). The ionisation potential is about 17 volts (Dingle, Proc. Roy. Soc. 1926–27, A, **113**, 323).

Fluorine is diamagnetic. Its specific susceptibility and atomic susceptibility, deduced from measurements on fluorinated organic compounds, are $-0{\cdot}345\times10^{-6}$ and $-6{\cdot}55\times10^{-6}$ respectively (Pascal, Bull. Soc. Chim. 1911, [iv], **9**, 7; 1912, [iv], **11**, 117, 204). The magnetic moment, measured by the molecular beam method, is 2·635±0·014 nuclear magnetons (Rabi, Millman, Kusch and Zacharias, Physical Rev. 1938, [ii], **53**, 495). The dielectric constant of liquid fluorine varies from 1·556 at −183·6° to 1·487 at −185·5° (Kanda, Bull. Chem. Soc. Japan, 1937, **12**, 473). The surface tension of liquid fluorine varies from 14·61 at −216·0 to 9·85 at −188·2° (Kanda, *ibid.* 469).

The boiling-point was determined as −188·2°, which agrees with a later value of −188° (Aoyama and Kanda, Bull. Chem. Soc. Japan, 1937, **12**, 416). The melting point is −217·8°, and on cooling below this temperature the solid changes in colour from yellow to white at −253°. The heats of vaporisation and of fusion are 1,436 and 340 g.-cal., respectively. Cady and Hildebrand (*l.c.*) determined the critical temperature directly as −129°, corresponding to a critical pressure of 55 atm. The entropy of fluorine is 48·6 g.-cal. per degree at 25° and 1 atm. (Garner and Yost, J. Amer. Chem. Soc. 1937, **59**, 2738). The density of liquid fluorine is 1·14 at −200° and 1·108 at the boiling point.

The vapour pressure of fluorine was measured by Cady and Hildebrand (J. Amer. Chem. Soc. 1930, **52**, 3839). The following are some of their values:

Temperature (Abs.)	Vapour Pressure (cm.)
72·53	14·54
75·88	23·83
78·96	36·68
81·19	49·32
84·13	68·64
85·99	85·50

Liquid fluorine is not miscible with liquid air. A saturated solution of chlorine in liquid fluorine at −195° contains 1·04% of chlorine (Aoyama and Kanda, Bull. Chem. Soc. Japan, 1937, **12**, 455).

Various values are given in the literature for the normal potential of the fluorine electrode. Neumann and Richter (Z. Elektrochem. 1925, **31**, 481) obtained values between 1·91 and 1·93 volts from measurements on the fused fluorides of lithium, sodium, potassium, calcium, strontium, barium, magnesium and beryllium. Abegg (*ibid.* 1903, **9**, 569) gives a value of 1·96 volts, but Latimer (J. Amer. Chem. Soc. 1926, **48**, 2868) obtained the value 2·85±0·04 volts from thermal data. The mobility of the fluoride ion at 25° is 40·2 and 54·4 in methyl alcohol and water, respectively (Hartley and Raikes, Trans. Faraday Soc. 1927, **23**, 393).

REACTIONS OF FLUORINE.

The great reactivity of elementary fluorine has resulted in the preparation of a large number of derivatives. Methods of fluorination other than those involving the direct action of the element are known, and will be described in some detail later (p. 278*c*). The reactions outlined below are those of fluorine itself, and the properties of the reaction products are referred to in detail only in a few instances of special interest. A full account of the metallic and non-metallic fluorides is given under the general chemistry of the element in question.

Fluorine and hydrogen were said by Moissan and Dewar to react explosively, even when solid fluorine was mixed with liquid hydrogen at −252°. v. Wartenberg and Fitzner, however (Z. anorg. Chem. 1926, **151**, 313), observed considerable induction periods in the reaction of the two gases at approximately 20°. Bodenstein and Jockusch (*ibid.* 1937, **231**, 24) also found that fluorine and hydrogen scarcely reacted at room temperature in a magnesium vessel. In platinum the reaction was explosive at room temperature but slow at −80°. These authors suggested that the reaction took place by a chain mechanism in which fluorine atoms played a part. Aoyama and Kanda (Bull. Soc. Chem. Japan, 1937, **12**, 521) confirmed that solid fluorine reacted explosively with liquid hydrogen, but found that such mixtures were stable in fine capillaries. Mixtures of the gases were stable in old glass vessels, and it was suggested that silicon tetrafluoride inhibited reaction.

Amorphous boron inflames in fluorine without the application of external heat and forms the gaseous fluoride, BF_3. Carbon will also burn in fluorine, and, in 1890, Moissan isolated the compound CF_4 in an impure state from the reaction products. Ruff and Keim (Z. anorg. Chem. 1930, **192**, 249) prepared the pure tetrafluoride (b.p. −130°) by the same reaction and showed that the fluorides C_2F_6, C_3F_8 and probably other members of the series up to C_6F_{14} are formed simultaneously. It is noteworthy that the fully fluorinated ethylene derivative C_2F_4 (b.p. −76·3°) is not formed in this reaction, but has been obtained by burning a carbon arc in carbon tetrafluoride and fractionating the product. A solid carbon monofluoride $(CF)_n$ is formed when "*Norit*," an activated carbon, is heated at 280° and 25 mm. pressure in a stream of fluorine. The swelling of carbon anodes used in the electrolytic preparation of fluorine is due to the formation of the solid monofluoride. This compound, which has an ionic lattice, decomposes when heated and forms a mixture of carbon fluorides, together with free carbon.

Silicon burns to the tetrafluoride in a stream of fluorine. There is no direct reaction between fluorine and nitrogen, although nitrogen trifluoride, NF_3 (b.p. −119°) has been obtained by Ruff, Fischer and Luft (*ibid.* 1928, **172**, 417) by the electrolysis of fused anhydrous acid ammonium fluoride, $(NH_4)HF_2$, in an electrically heated copper cell at 125°. Unlike nitrogen trichloride this compound has a positive heat of formation and is comparatively stable. Thus, it is unchanged by dry glass, water or dilute alkalis. It explodes when mixed with hydrogen and sparked.

Phosphorus and arsenic burn in gaseous fluorine, forming either the tri- or pentafluorides. Sulphur also burns in fluorine. Moissan and Lebeau isolated the hexafluoride SF_6 (v.p. 1 atm. at 62°) from the products, and recently Denbigh and Whytlaw-Gray (J.C.S. 1934, 1346) isolated a second fluoride of the composition S_2F_{10} from the less volatile fractions of the fluorination products from sulphur. It is believed that two other sulphur fluorides, SF_2 and S_2F_2, also exist, but they are not formed directly from the elements. Selenium and tellurium also react very readily with fluorine, the final products of reaction being the hexafluorides SeF_6 and TeF_6.

Reaction of Fluorine with Metallic Elements.—The reaction of fluorine with the metallic elements is, as a rule, vigorous and yields the metallic fluorides. Sodium and potassium inflame if exposed to the gas at room temperature. Calcium and magnesium are attacked at room temperature with great evolution of heat. Lead is attacked vigorously in the cold, but with metals such as mercury, aluminium, iron, chromium and manganese attack at room temperature is limited to the formation of a surface film, and a certain amount of external heat must be applied in order to obtain further reaction. Bismuth suffers only a superficial attack by fluorine, even at a red heat. Copper and gold are likewise attacked extensively only at a red heat. Silver is attacked slowly in the cold: at 100° the metal becomes covered with a yellow film of the anhydrous fluoride. At a dull red heat reaction occurs with incandescence. Osmium burns in fluorine when heated above 250°, but palladium, iridium and ruthenium are attacked only at a red heat. Platinum is strongly attacked at 500–600°, reaction being accelerated by the presence of hydrogen fluoride.

The majority of the metallic compounds of fluorine are easily fusible, and when ignited in a current of steam many of them are converted into the corresponding oxides, whilst hydrofluoric acid is formed. The fluorides of silver and tin are easily soluble in water, whilst those of sodium, potassium and iron are only sparingly soluble. They are all decomposed when heated in sulphuric acid, with evolution of hydrofluoric acid. Solutions of the soluble fluorides corrode glass, and they give no precipitate with silver nitrate, as the fluoride of silver is soluble. Lead, barium, magnesium and calcium salts produce insoluble precipitates. Many metallic fluorides combine with hydrofluoric acid to form acid fluorides, the most familiar examples of which are the acid fluorides of potassium which are used in the electrolytic preparation of the element.

Action of Fluorine on Various Inorganic Compounds.—Moissan observed that fluorine displaces the other halogens from hydrogen chloride, bromide or iodide. Hydrogen sulphide was also decomposed with inflammation, sulphur fluorides and hydrogen fluoride being formed. Ammonia was found to burn in an atmosphere of fluorine to give free nitrogen and hydrogen fluoride (Moissan, Ann. Chim. Phys. 1891, [vi], **24**, 249). Thionyl chloride was converted by fluorine to thionyl fluoride, and phosphorus pentoxide was attacked at a dull red heat and formed a mixture of phosphorus trifluoride and oxyfluoride. Arsenious oxide was also violently attacked, but Moissan, to whom these observations are largely due, did not isolate the products. He reported that fluorine was without action on the oxides of carbon, but according to Humiston (J. physical Chem. 1919, **23**, 572) carbon monoxide is decomposed in the presence of active carbon with formation of carbon fluorides. Phosgene reacts with fluorine and Humiston (*l.c.*) suggested that the product was carbonyl fluoride. This compound (b.p. −83°) has been prepared in a pure state by Ruff and Miltschitzky (Z. anorg. Chem. 1934, **221**, 154) by passing carbon monoxide over silver difluoride, AgF_2. It was found by these authors that carbon monoxide and fluorine reacted explosively when sparked.

Dry silica is not attacked by fluorine in the cold, nor is dry glass appreciably attacked, provided the gas is free from hydrogen fluoride. The reaction of fluorine with metallic oxides was studied by Moissan (*l.c.*); the product consists of the metallic fluoride, mixed in some cases with the oxyfluoride. It was found to be necessary as a rule to heat the oxide more or less strongly in order to initiate reaction.

Moissan's studies on the reactions of gaseous fluorine included qualitative observations with a large number of inorganic compounds. Chlorides, bromides and iodides of a number of metals and non-metals were attacked with displacement of the halogen and the formation of a fluoride. Cyanogen was found to burn in fluorine, and cyanides, ferrocyanides and thiocyanates were completely decomposed, either in the cold or on warming gently. Potassium sulphate was decomposed at a red heat, but under the same conditions potassium nitrate was unattacked. Phosphates were more readily attacked than were sulphates, and the carbonates of sodium, calcium and lead became incandescent when exposed to a stream of the gas. Borates of the alkali metals were found to resist the action of fluorine, even at a dull red heat, but other borates were attached more readily.

Interhalogen Compounds Containing Fluorine.—The formation of interhalogen compounds is most pronounced in the case of those members of this group which contain fluorine. Binary compounds of the composition ClF (b.p. −100°) and BrF (b.p. 20°) are known. Chlorine monofluoride, which is almost as reactive as fluorine itself, is formed when the elements are heated together at 250° (*cf.* Chem. Soc. Annual Rept. 1933, **30**, 129). Bromine monofluoride is formed when bromine is saturated with fluorine at 10°. It is less stable than the chlorine compound, and readily disproportionates into bromine and bromine trifluoride. Treatment of chlorine or its monofluoride with excess of fluorine at 250° yields the trifluoride, ClF_3 (b.p. 13°), which, like the monofluoride, is an extremely reactive substance. It is prepared and manipulated in apparatus constructed entirely of copper. Bromine trifluoride (b.p. 127°) is also formed from the elements. The pentafluorides of bromine and iodine have boiling points 40·5° and 97°, respectively. The first is formed from the elements at 200°. The iodine compound, IF_5, was first prepared by Gore by heating iodine and silver fluoride (Phil. Mag. 1871, [iv], **41**, 309). Moissan obtained it from the elements. The only other known compound of this type containing fluorine is the heptafluoride, IF_7, which was prepared by Ruff and Keim by the fluorination of iodine pentafluoride (Z. anorg. Chem. 1930, **193**, 176). Ruff and his co-workers are responsible for most of the investigations in this field.

Oxidising Properties of Fluorine.—Reaction of fluorine with water yields oxygen and hydrogen peroxide (Lebeau and Damiens, Compt. rend. 1927, **185**, 652; 1929, **188**, 1253). These authors claim that earlier reports of the formation of ozone in this reaction are attributable to the presence of fluorine monoxide in the fluorine. These reactions will probably account for the marked oxidising action of fluorine on a variety of aqueous solutions. Fichter and his collaborators have carried out numerous investigations in this field. Thus, for example, they have observed the conversion of cobaltous salts to salts of tervalent cobalt (Helv. chim. Acta. 1926, **9**, 1093). Manganese dioxide is precipitated from a solution of manganous sulphate by the action of fluorine, or, if a sufficient concentration of sulphuric acid be present, permanganic acid is formed. Addition of a fluoride or of free hydrofluoric acid to an electrolyte also facilitates anodic oxidation. Thus Skirrow (Z. anorg. Chem. 1902, **33**, 25) obtained greater yields of chromic acid by electrolysing chromic sulphate in presence of hydrofluoric acid than in presence of sulphuric acid. Increased yields are also obtained in the electrolytic preparation of persulphates by the addition of a soluble fluoride (Müller, Z. Elektrochem. 1904, **10**, 753, 776).

Fluorine Oxides.—Fluorine forms two oxides, F_2O and F_2O_2. The first of these compounds, *fluorine monoxide*, was discovered in 1927 by Lebeau and Damiens (Compt. rend. 1927, **185**, 652). It was formed, together with fluorine and oxygen, in the electrolysis of the molten acid fluoride $KF,2HF$ when the latter contained small amounts of water. An improved method developed by the same authors (*ibid.* 1929, **188**, 1253) consists of bubbling fluorine through 2% aqueous sodium hydroxide solution. The reaction is:—

$$2F_2+2NaOH=2NaF+F_2O+H_2O$$

The monoxide may be obtained in a 70% yield, and is purified by fractional distillation. The boiling point and melting point are −144·8° and −223·8°, respectively. The oxide is decomposed by solutions of alkalis with liberation of oxygen. It is a very reactive gas and is decomposed when heated with the majority of metals, forming a mixture of the metallic oxide and fluoride. It explodes when sparked with hydrogen or when heated with chlorine. One of the most striking facts about fluorine monoxide is that it is not itself explosive, as is chlorine monoxide. The heat of formation is variously given as −4,600 g.-cal. ± 2,000 g.-cal. (Ruff and Menzel, Z. anorg. Chem. 1930, **190**, 257) and −11,000 g.-cal. ± 2,000 g.-cal. (von Wartenberg and Klinkott, *ibid.* 1930, **193**, 409). Fluorine monoxide has strong oxidising properties; thus it will oxidise benzene to hydroquinone and quinone. The gas is slightly soluble in water (6·8 c.c. per 100 c.c. at 0°), but the solution does not have the acidic properties to be expected in a solution of hypofluorous acid. Hypofluorites are not formed on treating solutions of alkalis with fluorine monoxide. The aqueous solutions have, however, strong oxidising properties (*e.g.* $Cr^{\cdots}\rightarrow CrO_4''$).

The *fluorine oxide* F_2O_2 was first prepared by Ruff and Menzel (*ibid.* 1933, **211**, 204) by pumping an equimolecular mixture of fluorine and oxygen at a pressure of 15–20 mm. through a quartz discharge tube cooled in liquid air. The oxide separates as a yellow solid which decomposes into its elements at temperatures above −100°. It was formerly thought that the decomposition yielded a new oxide, FO, but this conclusion is now known to be erroneous.

Oxyacids of Fluorine.—The two acids **HFO** and **HFO_3** are at present unknown, although there are certain indications that their salts exist. Thus, although it has already been seen that fluorine does not form an acid solution in water, the action of fluorine on 50% potassium hydroxide solution at −50° gives a product which, even after evaporation and fusion of the residue, has marked oxidising properties, which are probably due to a hypofluorite or a fluorate (Dennis and Rochow, J. Amer. Chem. Soc. 1933, **55**, 2431). It has also been observed that when a molten mixture of potassium hydroxide and potassium fluoride is electrolysed in a silver crucible, which serves as cathode, and with a graphite rod as anode, the product probably contains a certain amount of fluorate.

Reaction of Fluorine with Organic Compounds.—The reaction of free fluorine with organic compounds is, in general, violent. Moissan's observations (*cf.* "Le Fluor," 1900) showed that carbon tetrafluoride and carbon are common products. Various alcohols were shown to inflame at room temperature. Ethyl acetate was attacked, as were various halogenated carbon derivatives. Paraffin was attacked when slightly warmed, and Humiston (J. physical Chem. 1919, **23**, 572) showed that, with acetone, explosions were liable to occur even when the reactants were cooled to −80°. The same author attempted to moderate the action of fluorine by dilution with nitrogen, and this method appears to offer a means of using gaseous fluorine as a fluorinating agent.

In recent years methods for the direct fluorination of organic compounds have been developed, although the use of one or other of the fluorinating agents described in the next section is more common. Thus, for example, Calfee and Bigelow (J. Amer. Chem. Soc. 1937, **59**, 2072) were successful in fluorinating ethane directly over a copper gauze catalyst by a continuous process. A good yield of hexafluoroethane was obtained, together with carbon tetrafluoride and a small amount of a product which was believed to be methyl fluoroform. Hexachloroethane and fluorine react under similar conditions and give a 20% yield of *s*-$C_2Cl_4F_2$ (Miller, Calfee and Bigelow, *ibid.* 1937, **59**, 198). This method of fluorination was suggested by Fredenhagen and Cadenbach (Ber. 1934, **67** [B], 928); they found that for fluorination in the gas phase dilution with at least 15 vols. of nitrogen was necessary if inflammation was to be avoided. Various liquids (*e.g.* toluene, cresol or hexane) were fluorinated by allowing fluorine diluted with nitrogen to pass over the liquid surface, while a fluorinated derivative of palmitic acid (21%F.) was obtained by similar treatment of a carbon tetrachloride solution of the acid. An alternative method is to dissolve the material to be fluorinated in hydrogen fluoride, or a fluorinated hydrocarbon, and to expose the liquid to the action of fluorine in presence of a catalyst such as antimony pentachloride. Benzene when fluorinated in this way in hydrogen fluoride solution at −70° gave a product containing 45 per cent. of fluorine (E. I. Du Pont de Nemours and Co., B.P. 429591).

Fluorinating Agents.—The possibility of fluorinating organic compounds by the action of fluorides was realised in the last century by Swarts (Bull. Acad. roy. Belg., 1892, [iii] **24**, 309, 474), who used antimony trifluoride in presence of antimony pentachloride or bromine for this purpose. This gave a ready means of replacing chlorine or bromine atoms in organic molecules by atoms of fluorine (*see also* Swarts, Bull. Soc. Chim. 1924, [iv], **35**, 1557). This method has been applied recently in the preparation of a range of volatile compounds, some of which (*e.g.* CCl_2F_2 and CCl_3F) have been applied in refrigeration plant. Thus, fluorine may be substituted for chlorine in carbon tetrachloride with great ease by treating the tetrachloride with antimony trifluoride in presence of antimony pentachloride and a yield of about 90% of CCl_2F_2 may be obtained. This difluoride, which boils at −30° does not corrode metals and is non-inflammable and of low toxicity. It is utilised in refrigeration plant (Midgley and Henne, Ind. Eng. Chem. 1930, **22**, 542). This substance and other partially fluorinated derivatives of CCl_4 are also claimed as useful components of fire extinguishers. Midgley and Henne have obtained $C_2Cl_2F_2$ by passing carbon tetrachloride over calcium fluoride and antimony sulphate at 80°/55 lb. per sq. in., using a trace of antimony pentachloride as catalyst (U.S.P. 2013062, 1935). Henne has also described the use of chlorine as a catalyst for the fluorination of aliphatic halides (*e.g.* CCl_4 or C_2Cl_6) (U.S.P. 1990692, 1935). Numerous applications of antimony trifluoride in this field have been described (*see*, for example, Henne *et al.*, J. Amer. Chem. Soc. 1936, **58**, 402, 887; 1938, **60**, 864, 2491). Antimony trifluoride has also been used as a fluorinating agent for halogenated inorganic compounds. Here, again, the reaction proceeds smoothly. From phosphorus trichloride, for example, a mixture of PF_3, PF_2Cl and $PFCl_2$ was obtained (*cf.* Booth *et al.*, J. Amer. Chem. Soc. 1932, **54**, 4750; 1933, **55**, 3890; 1934, **56**, 1531; 1935, **57**, 1333; 1936, **58**, 63).

A number of alternative fluorinating agents are available. These include the fluorides of mercury, silver, thallium, lead and zinc, and, in addition, hydrogen fluoride itself. Thus, to quote these examples, Henne and Renoll (*ibid.* 1938, **60**, 1060) found that mercurous fluoride gives good yields of alkyl fluorides from the iodides or bromides. Schumb and Gamble used anhydrous zinc fluoride to prepare hexafluorodisilane from hexachlorodisilane. They note that this method is not satisfactory for the fluorination of hexachloroethane (*ibid.* 1932, **54**, 583). The fluorination of triphosphonitrile chloride, $P_3N_3Cl_6$, by means of plumbous fluoride was found to give a mixture of products, but this particular reagent was more suitable for the reaction than either zinc fluoride or silver fluoride. The use of hydrogen fluoride as a fluorinating agent is referred to in a later section.

HYDROGEN FLUORIDE, HF

Hydrogen fluoride is a liquid which boils at 19·5° and freezes at −83°. It forms a colourless gas with an irritating odour, and is freely soluble in water. The aqueous solution has acidic properties and is known as *hydrofluoric acid.* The anhydrous material has no acidic properties. Concentrated solutions of the acid were first prepared in 1771 by Scheele by the action of concentrated sulphuric acid on fluorspar. Its corrosive action on glass was, however, known in the seventeenth century.

Anhydrous hydrogen fluoride may be prepared from anhydrous potassium hydrogen fluoride, as already described (p. 273*d*). The preparation is rendered difficult by the great reactivity of the compound, by its hygroscopic nature and by the fact that it reacts chemically with dehydrating agents such as phosphorus pentoxide and sulphuric acid. Fredenhagen and Cadenbach (Z. anorg. Chem. 1929, **178**, 289) have published details of the preparation of the anhydrous fluoride for use in their studies on its solvent action. The last trace of water is given up by potassium hydrogen fluoride only after it has been heated to above 500°. Simons (J. Amer. Chem. Soc. 1924, **46**, 2175) has shown, however, that water can be removed completely from the acid fluoride by electrolysis. For a convenient laboratory method of preparing anhydrous hydrogen fluoride, *v.* Booth, *op. cit.*, p. 134.

The technical production of the anhydrous fluoride represents a relatively new development in this industry. It is bound up with the production of the concentrated aqueous acid, which is based on the interaction of fluorspar and concentrated sulphuric acid.

$$CaF_2+H_2SO_4=CaSO_4+2HF$$

The decomposition is effected in a leaden retort, divided into two halves for convenience in cleaning. These fit together by an accurately grooved joint. The receiver is also of lead, and should be cooled in a freezing mixture. Ruff and Braun (Ber. 1914, **47**, 646) recommend the use of 90% sulphuric acid. When 97–100% acid is employed a 60% yield of acid of 95–96% strength is obtained. With sulphuric acid containing 50–60% of sulphur trioxide the product consists of *fluorosulphonic acid* (*q.v.*), which is a thin colourless liquid, fuming in moist air.

$$CaF_2+H_2SO_4+2SO_3=CaSO_4+2HSO_3F$$

The above process for preparing hydrofluoric acid has been adapted for continuous operation. Thus, for example, the use of a rotating cylindrical retort has been described (U.S.P. 1842092; *see also* B.P. 462131, 1935). Acid containing between 95 and 99% of HF, which is a common product of the first distillation process, may be rendered anhydrous by distillation in a copper or iron vessel through a packed fractionating column at 15° (U.S.P. 2018397).

To prepare the aqueous solution on a large scale, a leaden retort, on the upper part of which a leaden head can be cemented, is used; the neck of the retort fits into the side of a leaden receiver or chamber, in which water is placed. The acid vapour is absorbed by the water, and air, with any excess of acid vapour, is passed into the atmosphere.

A difficulty in the preparation of hydrofluoric acid arises from the presence of silica in the fluorspar. This leads to contamination of the product with hydrofluosilicic acid, which is particularly undesirable if the acid is to be used in the manufacture of cryolite for the aluminium industry. Attempts have been made to separate silica by utilising the difference in densities (SiO_2, *d* 2·65; CaF_2, *d* 3·18). Alternatively, powdered fluorspar may be freed from silica by heating under pressure with caustic soda solution, when sodium silicate is formed (F.P. 612142, 1925). When fluorspar is treated with increasing quantities of concentrated sulphuric acid, silicon tetrafluoride is contained in the first distillate, and is dissolved in water and rejected (F.P. 540332, 1921).

The common impurities in the commercial acid are water, sulphurous, sulphuric and hydrofluosilicic acids and lead. Various methods of purification have been described. The impure acid may be purified by passing an excess of hydrogen sulphide through the liquid, neutralising the sulphuric and hydrofluosilicic acids present with potassium carbonate, then decanting and adding silver carbonate to remove excess of hydrogen sulphide. After filtering, the filtrate is distilled from a leaden retort with a platinum receiver and finally rectified. The anhydrous acid may be stored in copper vessels, which are, however, attacked by the aqueous acid. Platinum and lead vessels are also suitable. The dilute acid may be stored in lead or gutta percha, though the latter is slowly attacked (Maier, Chem.-Ztg. 1935, **59**, 1025). Ceresin bottles are now very commonly employed for storing the acid solutions.

Hydrofluoric acid prepared by the action of sulphuric acid on cryolite has the advantage that the starting materials may be obtained free from silica. Other methods of preparing hydrogen fluoride or its aqueous solution—which are, however, of little practical interest—are: by the direct union of the elements, by the action of hydrogen on the fluorides of lead or silver, and by the action of water on certain non-metallic fluorides.

Physical Properties of Anhydrous Hydrogen Fluoride.—Gaseous hydrogen fluoride is colourless. Its ultra-violet absorption spectrum consists of a series of bands, with a maximum absorption at λ2,800 A. (Siga and Plumley, Physical Rev. 1935, [ii], **48**, 105). The molecular refraction for the D line is 1·90 (Fajans and Joos, J. physical Chem. 1924, **23**, 1). The nuclear separation in the molecule is 0·864 A., the dipole moment of unassociated HF being 1·58 Debye units (Clark, Physikal. Z. 1934, **35**, 622). The dielectric constant is 174·8 at −73°, 134·2 at −42° and 83·6 at 0° (Fredenhagen and Dahmlos, Z. anorg. Chem. 1928, **178**, 272).

The vapour density of anhydrous hydrogen fluoride was measured by Thorpe and Hambly (J.C.S. 1889, **55**, 163). Their results for temperatures between 26·4° and 88·1° are tabulated below. The derived values of the molecular weight show a continuous change. The theoretical densities corresponding to the formulæ HF, H_2F_2 and H_3F_3 are 0·6908, 1·3816 and 2·0724, respectively.

Temperature °C.	Pressure mm.	V.D. Air=1.	Mol. weight.
26·4	745	1·773	51·18
27·8	746	1·712	49·42
29·2	750	1·578	45·54
32·0	743	1·377	39·74
33·1	750	1·321	38·12
33·8	758	1·270	36·66
36·3	739	1·115	32·20
38·7	751	1·021	29·46
39·2	743	1·002	28·94
42·8	741	0·910	26·26
47·3	745	0·823	23·76
57·5	750	0·737	21·28
69·4	746	0·726	20·96
88·1	741	0·713	20·58

Gaseous hydrogen fluoride is evidently associated, but there is no decisive evidence as to the molecular species present. It is commonly supposed that H_2F_2 is present, but the density can exceed considerably the value corresponding to this formula. Simons and Hildebrand (J. Amer. Chem. Soc. 1924, **46**, 2179) consider that the vapour is composed of an equilibrium mixture of HF and H_6F_6. Fredenhagen (Z. anorg. Chem. 1934, **218**, 161) showed that the vapour density of hydrogen fluoride at the boiling point corresponded with the formula $(HF)_{3\cdot5}$. This association factor was found to be 4·27 at −34° (Fredenhagen, *ibid.* 1933, **210**, 210).

The vapour pressure curve of hydrogen fluoride was examined by Gore (J.C.S. 1869, **22**, 368). Recently Claussen and Hildebrand (J. Amer. Chem. Soc. 1934, **56**, 1820) have represented the vapour pressures of HF and of its deuterium analogue in the pressure range 5–76 cm. by the following relationships:

$$HF:\ \log_{10}p(\text{cm.})=6{\cdot}3739-1316{\cdot}79/T$$
$$DF:\ \log_{10}p(\text{cm.})=6{\cdot}2026-1261{\cdot}16/T$$

The boiling point is 19·5° and the melting point −83° (Simons and Hildebrand, J. Amer. Chem. Soc. 1924, **46**, 2179). The molecular elevation of the boiling-point is 1·90 (Fredenhagen and Cadenbach, Z. physikal. Chem. 1933, A, **164**, 201). The latent heat of vaporisation is 97·5 g.-cal./g. (Simons and Bouknight, J. Amer. Chem. Soc. 1933, **55**, 1458).

The critical temperature of hydrogen fluoride is 230·2° (Bond and Williams, *ibid.* 1931, **53**, 34). The densities and surface tensions of the liquid in the ranges −75° to +5° and −80° to +19°, respectively are given by the relationships below, due to Simons and Bouknight (*ibid.* 1932, **54**, 129).

$$d=1{\cdot}0020-0{\cdot}0022625t+0{\cdot}000003125t^2$$
$$\gamma=40{\cdot}7[1-T/_{503\cdot2}]^{1\cdot78}$$

Measurements of the specific heat of the solid and liquid have been carried out by Dahmlos and Jung for the temperature range −175° to 0° (Z. physikal. Chem. 1933, B, **21**, 317). For measurements with gaseous HF, *see* Clusius, *ibid.* 1930, B, **8**, 427.

The heat of formation of hydrogen fluoride is given by Wartenberg and Schütza (Z. anorg. Chem. 1932, **206** 65) as 64·45 kg-.cal. Ruff and Menzel (*ibid.* 1931, **198**, 375) give 64·0 kg.-cal. The heat of dissolution at a dilution of 1 mol. of HF in 400 mol. of H_2O is 11,560 g.-cal. (Wartenberg and Fitzner, *ibid.* 1926, **151**, 313).

Aqueous Hydrofluoric Acid—Anhydrous liquid hydrogen fluoride is miscible in all proportions with water. Densities of the resulting solutions are tabulated below (Domange, Compt. rend. 1934, **198**, 469).

Weight %	d^{15}
5·06	1·017
10·1	1·035
20·25	1·072
29·8	1·108
39·9	1·149
53·8	1·205

Cady and Hildebrand have studied the freezing points of these aqueous solutions (J. Amer. Chem. Soc. 1930, **52**, 3843), and have shown that the hydrates HF,H_2O, $2HF,H_2O$ and $4HF,H_2O$ are formed. A constant boiling mixture is formed with water, which boils at 110·8° under a pressure of 732 mm., and contains 38·18% of of HF (Muehlberger, J. physical Chem. 1928, **32**, 1888). Pranschke and Schwiete have recorded the specific heats of these solutions (Z. anorg. Chem. 1935, **223**, 225). Fredenhagen and Wellmann (Z. physikal. Chem. 1932, **162**, 454) measured the conductivity of aqueous solutions at dilutions of 0·5–10,000 litres, and found that the dilution law was not valid even at the highest dilution.

Anhydrous Hydrogen Fluoride as a Solvent.—Although anhydrous hydrogen fluoride has a low specific conductivity ($1{\cdot}4\times10^{-5}$ mho.) it is capable of dissolving numerous inorganic and organic compounds and the resulting solutions are in many instances good conductors. H. Fredenhagen (Z. anorg. Chem. 1939, **242**, 23) has shown that in addition to metallic fluorides, which dissolve with dissociation into metallic and fluoride ions, alkali-metal iodates and perchlorates also dissolve in anhydrous hydrogen fluoride without decomposition. By means of these solutions it was possible to precipitate thallous perchlorate from a solution of thallous fluoride in anhydrous hydrogen fluoride. Other perchlorates were also soluble, as was sodium sulphate. The latter could be used to precipitate silver sulphate from a solution of silver fluoride in hydrogen fluoride. Such ionic reactions are, however, limited to a few instances, and the majority of inorganic compounds are decomposed by anhydrous hydrogen fluoride.

Certain organic compounds also yield conducting solutions in hydrogen fluoride. These include substances such as alcohols, ethers, ketones, and organic acids, and it is thought that the ions in such conducting solutions are the fluoride anion and a complex cation formed by a combination of the organic molecule with the hydrogen ion. This mode of ionisation is illustrated by the examples below.

$$\begin{aligned}
&(C_2H_5)_2O &&+ HF \rightleftharpoons [(C_2H_5)_2O{\cdot}H]^{\bullet} &&+ F'\\
&CH_3OH &&+ HF \rightleftharpoons [CH_3OH{\cdot}H]^{\bullet} &&+ F'\\
&CH_3{\cdot}CO_2H &&+ HF \rightleftharpoons [CH_3CO_2H{\cdot}H]^{\bullet} &&+ F'
\end{aligned}$$

Evidence for this mode of ionisation is derived from measurements of the molecular conductivity and the molecular elevation of boiling point of the solutions. The alkyl fluorides do not give conducting solutions in anhydrous hydrogen fluorides while a number of organic compounds, among which are the saturated hydrocarbons, are practically insoluble (Klatt, Z. anorg. Chem. 1937, **234**, 189).

Chemical Properties of Hydrogen Fluoride.—Anhydrous hydrogen fluoride attacks the alkali and alkaline earth metals. Aluminium is attacked at 100°, and zinc, cadmium, iron, chromium and copper at a red heat. Platinum and gold are attacked at 1,000°. Aqueous hydrofluoric acid attacks all the metals with the exception of lead, gold and the platinum metals.

Other reactions of hydrogen fluoride have been somewhat incompletely studied, probably owing to manipulative difficulties. Sulphur trioxide is converted to fluorosulphonic acid (Thorpe and Kirmann, J.C.S. 1892, **61**, 921). Moissan found that phosphorus pentoxide and HF yield the oxyfluoride, POF_3 (Bull. Soc. Chim. 1891, [iii], **5**, 458). The anhydrous fluoride is said to attack finely divided, precipitated silica, but not quartz or sand. Schwarz (Z. anorg. Chem. 1912, **76**, 422) states that the different varieties of silica are attacked at different rates by the aqueous acid. Thus 5% acid gives 96·6% attack for amorphous silica, 76·3% for tridymite, 74·3% for cristobalite and 30·1% for quartz. The attack of the vapour of hydrofluoric acid "frosts" glass, while the aqueous acid produces a transparent etching effect (*vide infra*). It is claimed that glass is unattacked by rigorously dried hydrogen fluoride. Most of the metallic oxides are attacked by aqueous hydrogen fluoride, reaction being more marked when the fluoride of the metal in question is soluble in water. Von Haagen and Smith (J. Amer. Soc. Chem. 1911, **33**, 1504) have examined the action of gaseous hydrogen fluoride on certain metallic oxides (Al, rare earths, Ti, Zr, Th, Ta) and have found that fluorides are formed. A number of metallic and non-metallic halides are converted by hydrogen fluoride to the corresponding fluorides.

The action of hydrogen fluoride on organic compounds is as a rule violent. It is, however, finding applications as a fluorinating agent. Grosse and Linn, for example, have studied the direct addition of HF to olefinic compounds, and find such a reaction to be possible in a number of instances: thus ethylene, when it is heated to 90° under pressure with anhydrous HF will give an 80% yield of ethyl fluoride. Simons and Lewis (*ibid.* 1938, **60**, 492) obtained 75–90% yields of benzotrifluoride from benzotrichloride and gaseous hydrogen fluoride. Again, hydrogen fluoride in presence of a catalyst has been used to obtain fluoroparaffins from other halogenoparaffins (U.S.P. 2062743, 1936). Simons and Archer (J. Amer. Soc. Chem. 1938, **60**, 986) have also used hydrogen fluoride as a condensing agent: thus, in presence of HF at 0°, C_6H_6 with C_3H_6 gives $PhPr^{\beta}$.

Use of Hydrofluoric Acid.—The oldest use of this compound is in etching glass. In making the graduations on a thermometer the tube is first coated with engravers' etching varnish; the divisions are then accurately traced with a fine-pointed instrument through the varnish. The tube is then plunged for a short time into a long tube containing dilute hydrofluoric acid, when, after cleaning the thermometer tube, it will be found to be permanently engraved. If the engraving is done by the vapour of hydrofluoric acid, the tracings are white and opaque, whereas, if the liquid acid be employed, the lines are transparent.

There are three processes in use for the preparation of opaque etchings on glass: viz. the application of (*a*) solutions of an acid fluoride of the alkalis; (*b*) a mixture of fluorspar with sulphuric acid; and (*c*) hydrogen fluoride gas. The following recipes illustrate the composition of five etching baths of type (*a*):

Water	1,000	100	1,000	1,000	1,000
Acid potassium fluoride . . .	250	—	—	—	—
Sodium fluoride .	—	—	40	250	—
Ammonium fluoride	—	—	—	—	1,000
Alkali fluoride . .	—	8	—	—	—
Hydrochloric acid .	250	—	—	160–175	—
Sulphuric acid . .	—	1	—	—	250
Glacial acetic acid.	—	—	50	—	—
Potassium sulphate	140	—	—	200	—
Ammonium sulphate	—	—	—	—	100

(The quantities are expressed in grams)

In practice an acetic acid solution of sodium fluoride is much used, and is prepared by dissolving 25 parts of sodium carbonate crystals in 5 parts of fuming hydrofluoric acid, and adding to 1 litre of this solution, after clarifying, 1 litre of glacial acetic acid. For light shades of etching, a single application of the acid is sufficient, but for deeper shades repeated applications are necessary, as is the case in etching landscapes, etc., on glass. An etched glass surface viewed by the microscope has the appearance of an aggregation of crystals. Smaller crystals are formed from concentrated solutions, and the smaller the crystals the more delicate is the etching. The strength of an etching solution must be varied according to the compound used, and regard must also be paid to the kind of glass to be operated upon. The application of gaseous hydrofluoric acid does not produce a uniform opacity, and is, therefore, not suitable for the production of opaque plates.

Reference has already been made to the application of hydrofluoric acid in the manufacture of synthetic cryolite for the aluminium industry. A further use which is likely to develop is to be found in the manufacture of fluorinated organic compounds, the production of which has already been described. The ultimate source of the fluorine for the preparation of fluorinating agents other than fluorine itself is either fluorspar or cryolite.

Antiseptic Properties of Fluorine Compounds.—W. Thompson found that the compounds of fluorine, such as hydrofluoric acid, the acid and neutral fluorides of sodium, potassium and ammonium, are effective as antiseptics. Free hydrofluoric acid retards the activity of yeast, 5·5 mg. per 100 c.c. of sucrose solution arresting fermentation. Potassium fluoride, up to the same strength, however, augments it (Effront, Bull. Soc. chim. 1891, [iii], **5**, 476). The free acid promotes the activity of diastase by retarding lactic and butyric fermentations (Effront, *ibid.* 1891, [iii], **4**, 337, 627; 1892, [iii], **6**, 786), and its application in brewing has been suggested (Just, J.S.C.I. 1902, **21**, 131). Acid ammonium fluoride is used for disinfecting rubber hose-pipes in breweries, as it is a powerful antiseptic and does not attack the rubber. Fluorides have also been used as preservatives for sweet wines and beer, but are now illegal (*v.* FOOD PRESERVATIVES).

Physiological Action of Fluorine and Hydrofluoric Acid.—Gaseous fluorine has an irritant action on the membranes of the eyes, nose and respiratory system. Its action on the skin is said by Ruff to resemble that of hydrofluoric acid (*v. infra*), while the effect of volatile fluorides is also said to be similar. Gaseous or aqueous hydrogen fluoride produces painful and slow-healing wounds on contact with the skin. The action of liquid anhydrous hydrogen fluoride is similar, but more vigorous. Burns produced by hydrofluoric acid vapour may be treated (as a first-aid measure) by the frequent application of dressings moistened with sodium bicarbonate solution. Fredenhagen and Wellmann (Angew. Chem. 1932, **45**, 537) recommend the application of a paste of magnesium oxide and glycerol, or, in severe cases, the subcutaneous injection of 20% aqueous magnesium sulphate. Inhalation of hydrofluoric acid vapour was found to be slightly irritant at concentrations as low as 0·015 mg. per litre (Machle and Kitzmiller, J. Ind. Hyg. 1935, **17**, 223).

Hydrofluosilicic Acid, H_2SiF_6.—Aqueous solutions of this acid are prepared by heating a mixture of sulphuric acid and fluorspar, sand or glass, and passing the evolved silicon tetrafluoride into water. The reaction taking place is:

$$3SiF_4+4H_2O=2H_2SiF_6+Si(OH)_4$$

Blockage of the silicon tetrafluoride inlet tube by gelatinous silica is avoided by placing its end under a layer of mercury and allowing the gas to escape into the water from the mercury surface. The water should be at 60–70°. The gelatinous solution is filtered, and concentrated by evaporation at a temperature below 40°. Above this temperature the acid itself vaporises with the water vapour. The acid may also be prepared by the action of aqueous hydrofluoric acid on silica, or by the decomposition of calcium fluosilicate with sulphuric acid.

Pure hydrofluosilicic acid cannot be obtained. In its aqueous solutions the equilibria $H_2SiF_6 \rightleftharpoons SiF_4+2HF$ and $SiF_4+2H_2O \rightleftharpoons 4HF+SiO_2$ are established. Dissociation of the acid, according to the first of these equations, takes place when attempts are made to concentrate the acid beyond a certain point. A solution containing 13·3% of the free acid may be distilled unchanged. Density measurements with solutions containing up to 34% of the acid have been made by Stolba (J. pr. Chem. 1864, [i], **90**, 193). The density of a 34% solution is 1·3162.

Bauer and Glaesner (Ber. 1903, **36**, 4209) have studied the distillation of aqueous solutions of the acid. Those containing more than 13·3% of acid, on evaporation, lose silicon tetrafluoride more rapidly than they lose hydrogen fluoride, and hydrolysis of the former produces silicic acid in the distillate. The distillate from a weaker acid contains free hydrogen fluoride. The dilute aqueous solutions of the acid are strongly hydrolysed. Strong aqueous solutions of the acid fume strongly, though the acid itself does not attack glass.

The salts of hydrofluosilicic acid (the *fluosilicates* or *silicofluorides*) may be obtained by the action of the aqueous acid on metallic oxides or carbonates, or by the action of silicon tetrafluoride on metallic fluorides (*see*, for example, B.P. 357922, 1931). They are soluble in water, except the salts of sodium, potassium and barium, which are very sparingly soluble ($BaSi_2F_6$, 1 part in 3,802 of H_2O). For details of solubilities and methods of analysis, *see* Worthington and Haring, Ind. Eng. Chem. [Anal.], 1931, **3**, 7.

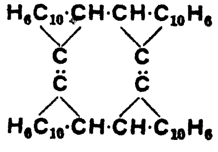
Fluosilicates are isomorphous with titanifluorides and stannifluorides. They evolve silicon tetrafluoride when heated, and when treated with concentrated sulphuric acid the free acid is liberated and dissociates into silicon tetrafluoride and hydrogen fluoride. Fluosilicates are decomposed by alkali into a silicate and a fluoride.

Fluosilicates have been employed in hardening calcareous stone surfaces. They are also applied as insecticides and for the preservation of timber (*cf.* Daric, Chim. et Ind. 1934, **31**, 1016; Pflug, Angew. Chem. 1932, **45**, 697). The fluosilicates possess more powerful antiseptic properties than do the fluorides. Both fluorides and fluosilicates are toxic and chronic poisoning may result from the presence of fluorides in drinking water. The solutions have only a very slight alkaline taste. The use of silicofluorides for food preservation is illegal.

For qualitative and quantitative methods of analysing fluorides and fluosilicates, *v.* CHEMICAL ANALYSIS, Vol. II, pp. 571*a*, 576*a*, 595*a*, 607*c*, 656*d*.

H. J. E.

FLUOROCYCLENE, $C_{48}H_{28}$. A hydrocarbon obtained in 30% yield by heating acenaphthene with PbO_2 at 200°. Crystallises in orange-yellow rhombohedra with violet-blue fluorescence, m.p. 396–397°. From its reactions with bromine and consideration of its absorption spectra the following formula has been proposed (Dziewoński and Suszko, Ber. 1925, **58** [B], 723).



FLUOROFORM, CHF_3, is obtained together with $CHIF_2$ and CHI_2F by heating at 80° a mixture of HgF, CHI_3 and CaF_2 (33·4:20:40) and fractionating the product at −30° to −40° at which temperature pure fluoroform is separated from the other two products, in yield about 45% of the theoretical (Ruff *et al.*, Ber. 1936, **69** [B], 299). Henne obtained a yield of 80% by warming a mixture of $CHBr_3$ with Br and excess SbF_3 at 4 atm. and treating the resulting $CHBrF_2$, after purification, with HgF_2 at about 50° under 12 atm. (J. Amer. Chem. Soc. 1937, **59**, 1200). Fluoroform has b.p. −84·4/760 mm. and m.p. −160°; it is almost completely chemically and physiologically inert.

FLUOR-SPAR. *Fluor*, or *Fluorite*. (Ger. *Flussspat*; Fr. *Fluorine*.) A common mineral composed of calcium fluoride (CaF_2), crystallising in the cubic system. It is frequently found as well-developed crystals, usually cubes, but occasionally as octahedra; interpenetrating twinned cubes are common. An important character is the possession of perfect cleavages parallel to the faces of the octahedron. Sp.gr. 3·18; hardness 4 (the mineral can be scratched with a knife). The crystals have a bright vitreous lustre, and are frequently transparent; they may be colourless or various shades of purple, green, yellow, pink, etc., the mineral displaying a very extensive range of colour. Dull cleavage masses and massive material, sometimes quite compact or earthy, are of abundant occurrence.

The cause of the colour of fluor-spar has long been a subject of discussion, and although not yet definitely determined, it may, in some cases at least, be ascribed to the presence of traces of organic matter. Some crystals undergo a change in colour when exposed to sunlight; for example, certain greens are changed to purple. Changes in colour are also effected when the crystals are exposed to the cathode rays, or to the rays emitted by radium salts. Many crystals are decolorised when heated to a temperature ranging from 220° to 300°. The heating of the mineral is usually accompanied by a bright phosphorescence (thermo-luminescence), violent decrepitation, and the liberation of water and gases (carbon dioxide, carbon monoxide, hydrogen, nitrogen, argon and oxygen). The water which distils off is sometimes brown, and has a strong " empyreumatic " odour; and it is on this account, together with the fact that the mineral is decolorised at a low temperature, that the colour has been ascribed to organic matter. It must, however, be remarked that the water and gases, and possibly also any organic matter present, are contained in the fluor-spar in vast numbers of cavities, usually of microscopic dimensions, but sometimes large enough to show a moving bubble when a crystal is turned about in the hand. A remarkable phenomenon, sometimes associated with the colour of fluor-spar, is that of fluorescence; this is best displayed by certain purple or green crystals from Weardale, Co. Durham. A crystal, which by transmitted light is pinkish or greenish, exhibits when viewed in reflected light a rich plum-blue colour with a velvety softness which has the appearance of being diffused immediately beneath the surface of the crystal. This effect is destroyed when the crystals are heated to 220 or 300°.

Fluor-spar occurs under a variety of conditions: in cavities in granite rocks, in veins of tin-ore, occasionally as a cementing material in sandstone, and most abundantly as an associate of lead-ore in veins traversing limestone. Some of the veins in limestone, consisting almost entirely of pure massive fluor-spar, have a thickness of 20 feet. The whole of the production in England, amounting at the present time to about 40,000 tons per annum, is from north Derbyshire, and Weardale in Co. Durham, where it is obtained chiefly as a by-product in lead-mining. Formerly, when there was little or no demand for fluor-spar, this mineral was thrown out on the waste heaps; and now that the material is of value, these extensive waste heaps are being worked over. A considerable amount, some 50,000 tons per annum, is mined in the United States, principally in southern Illinois and western Kentucky. Curiously, however, a large portion of the English fluor-spar is exported to America. Smaller quantities are obtained in Bavaria, Saxony, France and Spain.

The name fluor, from the Latin *fluo*, to flow, was used in the form *fluores lapides* by G. Agricola in 1529, and has reference to the use of this mineral as a flux in metallurgical operations. Within recent years, its application in this direction has been very considerably extended, and now large amounts are used in the manufacture of iron and steel, chiefly in the basic open-hearth process, and of ferrosilicon and ferromanganese. If not contaminated with too much silica (not over 3 or 4%), it acts better than limestone for fluxing; but it corrodes the furnace-linings, and the resulting slag contains less soluble phosphates than normally available for fertilisers. To some extent, fluor-spar is also used in iron and brass foundry-work, as it produces a greater fluidity in the metal; in the smelting of lead-, copper-, silver- and gold-ores; in the electrolytic refining of antimony and lead; and in extracting aluminium from bauxite. Other applications are in the glass and enamelling industries, and in the manufacture of opaline glass. In the form of sand, the mineral is used as a binding material in emery-wheels and carbon-electrodes, and for mixing with mortar and cement.

Owing to its low refractive index ($n_D = 1·43385$) and weak dispersion, clear and colourless fluor-spar is used with glass for the construction of the apochromatic lenses of microscope objectives, but material which is perfectly isotropic and sufficiently transparent and free from colour is difficult to obtain. A limited amount of suitable material can be obtained by decolorising by heat the clear purple fluorescent cubes from Weardale, Co. Durham; and small colourless cubes are abundant in the neighbourhood of Matlock, Derbyshire. Suitable material in sufficient quantity is said to be found in Illinois; and a very promising deposit has been prospected in the Transvaal, between Zeerust and Mafeking. Material suitable for optical use has also been obtained at Madoc in Ontario.

A special variety of fluor-spar, known as "Blue John," for which the Tray Cliff cavern near Castleton in Derbyshire has long been famous, has been much used for fashioning vases and other small ornamental objects. Although occasionally used as a faceted gem-stone on account of the delicate colouring, the mineral is much too soft for wear. Beads of fluor-spar have been found amongst prehistoric remains in North and South America.

Fluor-spar being the only common mineral containing fluorine in large amount (F 48·9%), is used for the preparation of hydrofluoric acid and other fluorine compounds. It is slightly soluble in hydrochloric acid and in solutions of alkali carbonates, and is readily decomposed by sulphuric acid even in the cold (on this depends its use for etching glass, a process in use long before the discovery of the element fluorine). Being almost the only substance not attacked by free fluorine, it was used by H. Moissan in the construction of his apparatus for the isolation of this element (*v.* FLUORINE).

References.—Special Reports on the Mineral Resources of Great Britain, Mem. Geol. Survey, 1916, vol. iv. Fluor-spar, Imp. Min. Res. Bur. London, 1921. On the fluor-spar deposits of Derbyshire, *see* C. B. Wedd and G. C. Drabble, Trans. Inst. Mining Eng. 1908, **35**, 501; on those of Weardale, *see* W. M. Egglestone, *tom. cit.* 236; a detailed list of fluor-spar localities in the north of England is given by J. M. Sweet, Min. Mag. 1930, **22**, 263–264. On American deposits, *see* H. F. Bain, Bull. U.S. Geol. Survey, 1905, no. 255; E. O. Ulrich and W. S. T. Smith, Prof. Paper, U.S. Geol. Survey, 1905, no. 36; H. Ries, "Economic Geology," New York, 1916. On fluorescence and thermo-luminescence, H. Haberlandt and K. Przibram, Sitzungsber. Akad. Wiss. Wien, Abt. IIa, 1933, **142**, 235; 1934, **143**, 151; E. Iwase, Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **22**, 233; 1933, **23**, 22; 1934, **23**, 153.

L. J. S.

FLUX. A term used in metallurgy for the material or mixture of materials used in the dry assaying and smelting of ores for the purpose of combining with earthy materials present and removing these as a fluid slag, or for combining with and removing impurities from metallic substances, or for any material which is fluid at a high temperature and protects metallic bodies from oxidation.

All ores contain gangue, either of an acidic (siliceous) or of a basic character which would generally remain unmelted, retain a considerable proportion of the metal and foul the furnace if a reducing agent were used alone in the treatment of the ore. In order to remove this gangue, it is necessary to add fluxes which will combine with it to form a slag fusible at the temperature of the furnace.

A distinction may be made between the fluxes which are used for assaying and those which are used on a large scale for smelting. The more important fluxes used in assaying are:

Sodium Carbonate used for fluxing silica or quartz yielding easily fusible and fluid silicates of the type $x\text{Na}_2\text{O}, y\text{SiO}_2$. It also acts as a desulphurising agent and is used for ores containing zinc and tin compounds forming sodium zincate and stannate respectively. Sodium bicarbonate, NaHCO_3, is sometimes employed instead of the carbonate but possesses only one-half the fluxing power of the latter.

Sodium Hydroxide, NaOH, occasionally used instead of sodium carbonate when the charge contains much tin.

Borax, $\text{Na}_2\text{B}_4\text{O}_7, 10\text{H}_2\text{O}$, used either calcined or as borax glass forms one of the most useful fluxes in dry assaying. It melts readily and dissolves earthy and metallic oxides forming fusible borates. It combines with siliceous materials to form a fusible slag which acts as a protection against oxidation.

Silica, SiO_2, is used in the form of sand in the case of basic or pyritic charges and reduces the corrosive action of the bases present on the crucibles employed.

Fluor-spar, CaF_2, is a neutral flux and is used especially in the presence of phosphates. It combines with silica and is a valuable solvent for barytes and gypsum.

As refining fluxes the following may be used:

Potassium Nitrate or nitre. This is largely used as an oxidising agent as it is decomposed on heating and yields a large volume of oxygen. It is especially useful when melting gold contaminated with such impurities as lead and copper.

Ammonium Chloride or sal-ammoniac is also used in purifying gold as it is decomposed by certain metals in a molten state forming metallic chlorides and liberating ammonia.

The fluxes used in large scale smelting operations are few in number, and it is essential to the economic success of a process that the cost of slag-producing materials should be as low as possible. An economy is frequently effected by using a mixture of ores containing different gangue minerals, for example, an ore with a siliceous gangue may be mixed in proper proportions with an ore with a basic gangue so that no additional flux is needed. In general, the character of the fluxes to be used must be decided by the nature of the ore in such a way that the furnace charge shall contain siliceous and basic constituents in the proportions required to form a fusible silicate containing two or more bases.

Fluxes used on a large scale are of three classes:

(1) **Acidic.**—Silica as quartz, sand, etc.: Natural silicates. Siliceous slags.

(2) **Basic.**—Lime or limestone is the most important, being used in enormous quantities in iron smelting. Dolomite is also sometimes used as a basic flux in the smelting of ores of copper, lead, etc.

(3) **Neutral.**—Fluor-spar. This is used when it is desired to increase the fluidity of a slag. It fluxes sulphates of calcium, lead and barium; calcium phosphate; silica, silicates, etc. It is frequently used in the electric-furnace manufacture of steel.

As a refining flux for metals on a large scale, sodium carbonate has become very important. This is due to its powerful chemical affinity for sulphur which it removes from molten iron, it has at the same time a refining action on the graphite in cast iron, a degasifying action on molten metals and a scouring effect which eliminates harmful non-metallic inclusions such as metallic oxides, silicates, etc.

In soldering operations fluxes are used to protect from oxidation the surfaces of metal to be soldered and also the solder itself and to dissolve any oxide actually formed, the most important of these are zinc chloride used in soft soldering and borax used in brazing operations.

C. O. B.

FLY AGARIC *v.* AMANITA MUSCARIA (Vol. I, 300*d*).

FOAMS. A foam is a system consisting of a concentrated dispersion of gas bubbles in a liquid. The gas bubbles may be macroscopic, microscopic or ultramicroscopic, whereas the layers of liquid which separate them are of micronic or sub-micronic dimensions. A foam may therefore be considered as a system of laminæ which enclose gas bubbles in their interstices. Such a system is similar in many ways to a concentrated emulsion, the dispersed component of the foam being air whereas that of the emulsion is a liquid.

THE FORMATION OF FOAMS.—Foams are generated when gases are agitated with liquids and, more readily, when gases are evolved within liquids. Pure liquids, however, never give foams of more than transient stability. Solutions or suspensions of most capillary-active substances such as the higher fatty acids and alcohols, gelatin, vegetable gums, proteins, etc., give foams readily on agitation with gases; some compounds capable of *raising* the surface tension of water also foam freely. Molecular solutions of inorganic substances give only extremely unstable foams.

TYPES OF FOAM.—The following is a rough classification of foams:—

(1) *Hydrophobic Foams.*—These are unstable systems which result from the agitation in water of surface-active organic substances not capable of forming a unimolecular surface film, *e.g.* amyl alcohol, butyric acid.

(2) *Hydrophilic Foams.*—This class comprises two broad categories.

- (*a*) Two-phase hydrophilic foams which are formed by the agitation of aqueous colloidal solutions of film-forming organic substances, *e.g.* saponin, soaps.
- (*b*) Three-phase hydrophilic foams which incorporate a finely divided solid, *e.g.* galena, with or without an additional surface-active or film-forming organic substance.

THEORY OF FOAM STABILISATION.—The liquid laminæ which make up a foam structure will tend to contract because of their surface energy. The reduction of surface tension which is attendant upon the introduction of capillary-active substances would therefore be expected to impart additional stability to these films and hence to increase the stability of the foam. Foulk (Ind. Eng. Chem. 1929, **21**, 815) points out that there is confusion in the literature between ease of formation of a foam and its stability. These two properties are not necessarily related. Foaming tendency is not easily measured, but the time required for a foam to subside is essentially a stability measurement.

The main attribute of a stable liquid film is that it possesses great "elasticity," that is, the solution of which it is composed shall have a readily variable surface tension (J. W. Gibbs, "Collected Works," Longmans Green, London, 1928, Vol. **1**, 300 ff.). For the counteraction of mechanical stresses which will result in local extensions or contractions, the film must be able to respond with corresponding rises and falls in the surface tension. When permanent differences in stress are imposed upon different parts of the film, the latter must be able to maintain corresponding differences in surface tension in its different parts. Solutions of many capillary-active substances possess this property of readily variable surface tension, which is most marked at those concentrations where the variation of surface tension with changing concentration is most rapid, and not at the minimum surface tension. In confirmation of the above hypothesis Bartsch found (Kolloid-Z. 1926, **38**, 178) that the foaming power of solutions of butyric, nonylic and caproic acids, and octyl, heptyl and amyl alcohols increased with increasing concentration over a low concentration range. At a certain concentration, however, which corresponded to the sharp diminution in the slope of the surface tension/concentration curve, increase in concentration was actually attended by a decrease in foaming power. With such strongly surface-active substances as saponin and sodium cholate, which are among the best known foaming agents, the foaming power completely disappears in saturated and supersaturated solutions.

CONDITIONS AT THE INTERFACE.—When an added substance lowers the surface tension of a liquid it must, by the Gibbs' Adsorption Isotherm, be concentrated at the interface. The isotherm may be expressed in the form: $U=-\frac{C}{RT}.\frac{d\sigma}{dC}$ where C is the concentration of the solute, U its excess at the interface and $d\sigma$ the surface tension change. In the case of surface-active substances, surface tension decreases with concentration and so U is positive. With other materials surface tension increases with concentration and a negative adsorption takes place. Foulk (*l.c.*) points out that both systems with positive and negative adsorption have a tendency to foam. The former are, however, by far the more important and these only need be considered here.

When the concentration of a surface-active compound is infinitely small, the surface layer will be composed entirely of solvent molecules. At saturation $d\sigma/dC$ will be zero and the surface layer will contain only molecules of the solute. At neither of these two extremes does foaming take place, but only at intermediate concentrations. The heterogeneous surface layer, consisting of molecules of both the surface-active substance and the solvent, appears to be an essential characteristic of a foaming liquid. This heterogeneity no doubt conditions the essential elasticity of the foam laminæ.

On these grounds it is easy to explain the fact that high members of the homologous series of alcohols, acids, etc., are not efficient foaming agents for water. These substances have a greater tendency to colloidal solubility and therefore give rise to the formation of homogeneous molecular aggregates at the surface layer. The lower members, on the other hand, show molecular solubility but have very low surface activity. The intermediate members show the optimum relation between heterogeneity of the surface film and surface activity. This is illustrated by the values in Table I taken from Bartsch (Kolloid-Beih. 1925, **20**, 5).

TABLE I.—MAXIMUM FOAM STABILITY FOR HOMOLOGOUS SERIES IN AQUEOUS SOLUTION.

Solute.	Optimum Conc. (Mols./litre).	Maximum duration of foam (seconds).
Ethyl alcohol . . .	0·28	5·0
Propyl alcohol . . .	0·34	11·0
*iso*Butyl alcohol . .	0·09	12·0
*iso*Amyl alcohol . .	0·036	17·0
tert.-Amyl alcohol . .	0·034	10·0
Heptyl alcohol. . .	0·0007	8·0
Octyl alcohol . . .	0·0003	5·0
Formic acid . . .	0·45	4·0
Acetic acid	0·20	8·0
Propionic acid . . .	0·25	11·0
Butyric acid . . .	1·00	18·0
Valeric acid . . .	0·015	9·0
Caproic acid . . .	0·0075	13·0
Heptylic acid . . .	0·0015	16·0
Caprylic acid . . .	0·00025	12·0
Nonylic acid . . .	0·00007	5·0

Only those organic liquids, such as oleic acid and turpentine, which are capable of spreading on a water surface act as foaming agents. The velocity of spreading is not comparable with the rate of increase of surface during the formation of the foam, and there is therefore no possibility of a homogeneous layer being formed.

THREE-PHASE FOAMS.—Solid substances (such as galena, zinc blende, carbon, etc.) which are not readily wetted with water and which therefore tend to migrate to a water/gas interface may be used as foaming agents for water. Their foaming power increases with degree of dispersion. Thus galena of particle size 120–200μ was found by Bartsch (Kolloid-Beih. 1925, **20**, 1) to increase the stability of a foam of an aqueous solution of amyl alcohol from 18 seconds to 60 seconds, whereas galena of particle size 50μ increased the stability to several hours. Hydrophilic powders such as quartz and feldspar are readily wetted by water and are thus incapable of foam stabilisation.

The stability of three-phase foams is greatly increased on the addition of an emulsifying agent. The optimum concentration of emulsifying agent increases with the fineness of division of the solid. Bartsch deduces from these observations that a mono- or di-molecular layer of orientated molecules of emulsifying agent binds the aqueous solution to the gas and to the surface of the solid. This orientated layer prevents the displacement of the adsorbed gas from the solid surface by the aqueous solution. Such foams are therefore built up of flocks of gas, liquid, and solid, bound together by the emulsifying agent.

Traube and Kieke (*v.* Bartsch, *l.c.*, p. 47) have shown that solid substances adsorb surface-active materials more readily from water, the greater is their contact angle with water, that is, the less readily they are wetted with water. Thus a measurement of the contact angle of a solid against water will give a measure of its power of stabilising foam, all other things being equal. The same authors showed that the foaming ability of a solid may be destroyed, if an insoluble substance is added to the system, which wets the solid phase more readily than does water (*e.g.* chloroform).

THE STABILITY OF FOAMS.

One of the chief differences as a general rule between foams and emulsions is the much shorter life period of the former. Although both systems are thermodynamically unstable the emulsion is capable of a closer approximation to thermodynamic stability. In most disperse systems the kinetic energy of molecules is an important factor in opposition to coalescence. In foams, however, this factor is negligible on account of their semi-rigid structure. On the other hand, the tendency towards a reduction in interfacial area through the agency of surface-tension forces is far more marked with foams than with stabilised emulsions. Although electrical forces play a part in the stabilisation of all disperse systems, their rôle is not so important in the case of foams where capillary forces apparently play a larger part. In consequence of all these factors it is usually necessary to express foam stability in seconds. Some lyophilic foams, however, persist for hours and, in exceptional cases, for days. The following table taken from Plateau, "Statique expérimentale et théorique des liquides soumis aux seules forces moléculaires," 1873, II, 12, gives the maximum stability observed for foams of different systems.

TABLE II.—MAXIMUM STABILITY OF FOAMS ACCORDING TO PLATEAU.

Substance.	Maximum stability.
Distilled water	7 seconds.
Nitric acid	1 second.
Saturated solution of tartaric acid	142 seconds.
Acetic acid	8 seconds.
Marseille soap	2 hours.
Domestic soap	90 minutes.
Potash rosin soap . . .	1 hour.
Saponin solution . . .	12 hours.
Albumin solution . . .	Several days.
Ferric acetate solution . .	24 hours.

Factors influencing Foam Stability.—Early workers ascribed foam stabilisation to conditions of low surface tension and high viscosity, but although these factors are important the effect of many other variables has to be taken into consideration. The factors conditioning the stability of a foam may be summarised as follows :—

(*a*) Vapour pressure of the liquid phase.
(*b*) The nature and concentration of the foaming agent.
(*c*) The nature of the gas/liquid interface.
(*d*) The influence of protective colloids.
(*e*) The influence of electrolytes.
(*f*) The viscosity of the liquid phase.

Some of these factors call for special discussion.

Vapour Pressure.—Stable forms can never be obtained with liquids of high vapour pressure. This explains why foaming does not take place in pure liquids, since in these the low surface tension conditions necessary for foam stabilisation are only obtained at temperatures near the boiling point. Any tendency to foam stability which might otherwise be displayed by a pure liquid is therefore nullified by the almost instantaneous evaporation of the film laminæ.

Nature of the Foaming Agent.—The necessary conditions of low surface tension and heterogeneous surface have already been discussed; the specific properties of the foaming agent, however, influence the stability and behaviour of the foam by other means. Since a surface-active material is adsorbed at the interface, the bulk of the material will be collected in the foam where its local concentration may be high. Owing to orientation of the adsorbed molecules in the case of soaps, etc., or to a tendency to gel formation as with saponin and other hydrophilic stabilisers, the adsorbed layer in the foam may form a sheath which, in the latter case especially, may be of considerable mechanical strength, exactly the same as in the stabilisation of emulsions by materials which also act as foaming agents. In some systems the elasticity and strength of the interfacial film has been demonstrated experimentally.

In many instances the hydrophilic substance collected at the interface is not, by itself, capable of membrane formation, but such a structure is produced by oxidation or coagulation, the large surface area aiding such reactions. It is well known, for example, that some proteins coagulate when exposed in thin layers to air.

Although this mechanism is probably not responsible for the initiation of frothing, the semi-solid structure thus set up is the primary cause of the abnormally high stability of foam stabilised by proteins and other similar substances.

Properties of the foam, such as the size of the bubbles and their elasticity, are probably influenced by the nature of the interfacial membrane. Thus soap bubbles are elastic, while those of saponin are rigid and crinkle on contraction. The addition of a very small amount of soap solution to saponin is sufficient to convert the foam to an elastic type.

The Influence of Electrolytes.—As with emulsions, very little is known of the rôle of the electrical charge in the stabilisation of foams, except in the simplest cases. Taggart (Phil. Mag. 1914, [vi], **27**, 297; **28**, 364) examined the cataphoretic migration of gas bubbles under different conditions and found that these were charged negatively in pure water, similarly to the analogous oil hydrosols. The velocity of spheres of air, oxygen and hydrogen in pure water was found to be about 4×10^{-4} cm./sec. per volt/cm. The addition of hydrogen ions reduced the potential to zero without reversing the sign of the charge. Trivalent cations, however, caused a charge-reversal. Surface-active compounds reduced the cataphoretic velocity.

Since gas bubbles are charged negatively with respect to water, their stability towards electrolytes depends on the valency of the cation and its ability to be adsorbed. Some results of Bartsch (Kolloid-Beih. 1924, **20**, 1), collected in Table III show that for hydrophobic foams, a precipitation series is obtained, similar to that for hydrophobic suspensions.

Table III.—The Concentration of Various Electrolytes which reduce the Foam Stability of a 0·0568 Molar Solution of Amyl Alcohol from 18 seconds to 15 seconds.

Electrolyte.	Concentration (millimols/litre).
Sodium hydroxide	30
Sodium chloride	1·0
$Na_2SO_4/2$	0·8
$H_2SO_4/2$	0·04
$BaCl_2$	0·05
$AlCl_3$	0·0005
Cinchonine hydrochloride	0·03

Lyophilic foams are affected by electrolytes only to a small extent. Bartsch explains this on the ground that the interfaces of these systems are of a semi-rigid character, consisting in many cases of a gel of the colloidal foaming agent. The mechanical stability so brought about is not readily affected by ions except in concentrations high enough to cause a salting-out effect. In some instances chemical reaction may take place between the colloid at the interface and a polyvalent cation, resulting in the formation of a compound of entirely different characteristics. Hydrophilic foams may be sensitised by the addition of surface-active hydrophobic foamers and so made susceptible to electrolytes. For example, a foam formed from 0·001% saponin solution may be sensitised by the addition of 0·5% of amyl alcohol.

Protective Colloids.—Protective colloids have the power of immunising lyophobic foams against the action of electrolytes. The " gold number " (*v.* Colloids, Vol. III, p. 287*b*) of the protective colloid expresses its protective action towards lyophobic foams, just as in the case of lyophobic sols. In cases where a solid foaming agent is present, protective colloids at a sufficiently high concentration will displace the agent from the interface and themselves act as stabilising agents. This phenomenon has found application in flotation practice (*v.* Flotation Process).

Viscosity.—Evidence for the influence of fluid viscosity upon foam stability is as unconvincing as in the case of emulsion stability. In a series of experiments by Bartsch an attempt was made to increase the stability of amyl alcohol foams by the addition of glycerol and glycol. The results were negative until concentrations of 60% were reached. Nevertheless there is a general impression that high viscosity promotes foam stability, but quantitative measurements are very difficult owing to the fact that the viscosity of the body liquid may be very different from that of the foam laminæ. Many examples of increase of foam stability due to the addition to the system of components of high viscosity may be more profitably discussed from the point of view of modification of the properties of the interfacial membrane.

Technical Applications of Foams.

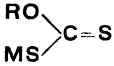
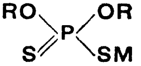
(1) *Beverages.*—The question of providing beer with a stable but not too fine-grained foam is of great importance in the brewing industry. The velocity of fermentation is an important factor in determining the stability of the foam (Freundlich, " Kapillarchemie," 1932, **2**, 828). It is not certain what constituents of beer act as foaming agents; proteins (Windisch and Bermann, Woch. Brau. 1919, **36**, 319; **37**, 109, 121, 137, 145, 153) and hop resins (Emslander, *ibid.* 1926, **43**, 418) are the most probable, but wheat gum and other dextrin-like substances probably increase the stability of the foam by modifying the properties of the membrane.

Lemonade and other " minerals " may be provided with a suitable foam by the addition of 0·01 g. of saponin to 1 litre of liquid.

(2) *Fire Extinguishers.*—For the smothering of small conflagrations, and especially those which involve burning oil or other organic liquids, devices which project a foam on to the surface of the burning material are frequently employed. These generally provide for the rapid generation of carbon dioxide in the presence of a solid foaming agent. It was formerly thought that the chemical nature of the carbon dioxide was responsible for the fire-quenching properties of the foam. Treichel (Chem.-Ztg. 1935, **53**, 69) has shown, however, that the effect is due to the foam laminæ which isolate the burning surface from the surrounding air; foams of air or even oxygen are equally effective (*v.* Fire Prevention and Extinction).

(3) *Flotation of Minerals.*—This subject is dealt with elsewhere in this volume, but a few words may be added here on the connection between foam and flotation. A quantity of finely ground ore is stirred with water, a foaming agent added and air blown in. A foam is formed on the surface of the liquid and the hydrophobic constituents of the ore are carried to and retained at the air/liquid interface, whereas the hydrophilic constituents sink as a sludge to the bottom of the vessel (*v.* section on Three-Phase Foams). The foaming agents are of two types:—

(*a*) Amyl alcohol, cresol, xanthates, etc., which themselves form the foam.

(*b*) Oleic acid, paraffin oil, naphthylamine, xylidine, etc., which are adsorbed by the hydrophobic particles and form " foam flocks." Such agents are called " collectors." Two of the most important series of " collectors " for sulphide minerals are the xanthates, of general formula  $\begin{matrix}RO\\MS\end{matrix}\!\!>C{=}S$ and the "*Aerofloats*" (Petersen, Kolloid-Z. 1932, **58**, 121), of formula,  $\begin{matrix}RO\\S\end{matrix}\!\!>P<\!\!\begin{matrix}OR\\SM\end{matrix}$ (R is an alkyl group and M a metal or other base usually alkali metal). These materials, which need only be used in small amounts, appear to be bound to the sulphide surface by chemical forces. There is evidence (Lintern and Adam, Trans. Faraday Soc. 1935, **31**, 564) that a surface oxidation of the ore is essential for the chemisorption of these " collectors."

(4) *Detergent Action of Foams.*—The use of foams of soap and other surface-active materials as detergents, involves a reversed application of the flotation process. Particles of dust or other impurities adhering to a surface, migrate to the foam interface if they are hydrophobic; when the foam is removed the impurities are carried with it. Emulsification and peptisation processes are, of course, also involved in the detergent action of soaps.

(5) *Liquid/gas Reactions in Foam Systems.*—It is a fact of technical importance that the reaction velocity of a gas with a liquid is markedly increased when the reactants form a foam system. A reactive gas reacts the more quickly with a liquid, the finer are the bubbles of the foam. Very fine bubbles may be produced (Coehn, Z. Elektrochem. 1923, **29**, 1, 306) by forcing the gas through a filter whose potential is of the same sign as that of the bubbles. For negatively charged bubbles, which are formed in the vast majority of cases, clay filters are suitable. Biesalski (Z. angew. Chem. 1928, **41**, 853; Biesalski, von Kowalski and Wacker, Ber. 1930, **63** [B], 1698) rapidly hydrogenised many organic compounds in aqueous solution by adding saponin to the liquid and blowing a stream of hydrogen bubbles through it. In a similar manner he was successful in completing the catalytic reaction of oxygen and hydrogen by metal sols at room temperature.

Prevention of Foaming.

It frequently happens in individual processes that foams are formed when their presence is undesirable. In the heat treatment of emulsified oils, for example, the tendency to foam is inconvenient, if only for mechanical reasons, while foams formed in the coating of paper may cause the bath of coating mix to overflow and make it difficult to observe whether the rollers are dipping completely into the mix and a paper with a heterogeneous surface may be produced. Other objectionable foams are met with in the dehydration of tars and in steam distillation.

The methods utilised for the suppression of foams may be divided into two main classes. The first involves the use of physical means and the second the use of the so-called "anti-froths."

(*a*) *Physical Methods.*—A frequent device is to place a superheating system above the surface of the liquid. The high vapour pressure which is set up in any liquid coming in contact with the heating element is sufficient to prevent foam formation.

If the liquid is treated in a confined space or under applied pressure, foaming is prevented to a large degree. This technique has been applied to the dehydration of emulsified crude oils.

Foam which arises in the course of vacuum distillation may be broken by passing the distillate between a series of heated gratings (Knichalik, G.P. 522782).

By passing a liquid to be distilled over a series of vertically suspended plates, a current of vapour returning to the main liquid surface inhibits foaming (Spilker, G.P. 506545).

(*b*) *The Use of Anti-Froths.*—It is not possible to lay down any rules for the choice of an anti-froth for a particular system. It frequently happens that a substance which inhibits frothing in one system is completely ineffective in another. Ether, for example, destroys beer froth instantaneously but has no effect on foaming glue, whilst milk, which itself foams, is an excellent anti-froth for glue. For a full discussion of anti-froths, *see* Meyer (Farben-Ztg. 1930, **36**, 481, 573 and 619).

One of the oldest industrial anti-froths is milk, but in paper coating, grease spots may be produced unless skim milk is employed. Sometimes the milk is allowed to become acid and the clear filtrate used as an anti-froth. The anti-froth action of milk is strongest in faintly acid or neutral media such as glue, gum arabic, etc.; in alkaline solution it is not effective. It is generally supposed that the anti-froth properties of milk are due to its fat content. Casein, produced from milk, does not foam because of a small fat content and is itself capable of suppressing the frothing of glue.

Many oils have been used as anti-froths, for example, butter, lard, poppyseed oil, peanut oil, whale oil, etc., and artificially prepared highly-dispersed emulsions of fats are generally superior to milk for this purpose. These are often unsuccessful, however, owing to interaction between the emulsifying agent and a constituent of the system the frothing of which has to be prevented; this may result in breakdown of the emulsion and separation of free oil.

Although glycerin is used to increase the stability of foams, the crude material is sometimes used as an anti-froth owing to traces of fatty acids or fats. Alkyl lactates are efficient in reducing both soap and glue foams. Amyl alcohol is a useful anti-froth, especially in cases where fatty materials cannot be used.

Bone fat produced by benzene extraction is an excellent anti-froth, but cannot be obtained on a large scale as it is used by glue manufacturers themselves to prevent undue foaming during boiling. Frothing of many industrial mixes is closely related to the p_H value of the system and the addition of a substance which alters this property has a corresponding effect on the foam. Among other anti-froths may be mentioned castor-oil soap, calcium and barium ricinates, petroleum and chlorine (for sewage).

Bibliography.—Chapter on "Schäume" in Freundlich, "Kapillarchemie," Vol. II, 1932; Berkman and Egloff, Physical Chemistry of Foams, Chemical Reviews, 1934, **15**, 377; N. K. Adam, "Physics and Chemistry of Surfaces," 2nd Ed., Oxford Uuiv. Press, 1938.

A. K.
D. F. C.

FOBBING *v.* Brewing (Vol. II, 95*d*).

FŒNUGREEK. The seeds of *Trigonella Fœnum-græcum* Lin. (Fam. Leguminosæ), an annual herb indigenous to West Africa and cultivated largely in India, Egypt and Morocco. The seeds are oblong-cylindrical and obliquely truncated at each extremity. They appear somewhat compressed, and are brownish-yellow in colour, 5–7 mm. long and 2 mm. thick. The seeds are widely used in veterinary practice, and P. Blum (Répertoire pharm. 1924, **35**, 185; Yearbook of Pharmacy, 1924, 324) claims that the stimulating and weight-increasing action of the seeds is at least equal to that of cod-liver-oil. He also mentions that the distinctive odour develops only on drying the seeds and that it is not present originally. The seeds are also employed as a condiment in curry powder.

Microscopic Appearance.—The palisade epidermis of the seed coat is composed of cells, which are about 5 times as long as they are wide, whilst the cells of the sub-epidermal layer show a distinct hour-glass appearance. The cells of the endosperm contain mucilage and those of the cotyledons aleurone grains and fixed oil.

Chemical Composition.—According to the British Pharmaceutical Codex the seeds contain about 28% of mucilage, 6% of fixed oil, and 22% of proteins. The ash should not be more than 5%. E. Jahns (Ber. 1885, **18**, 2518; 1887, **20**, 2840) has shown that the seeds contain choline and trigonelline, $C_7H_7NO_2$, which is probably identical with the betaine of pyridine-2-carboxylic acid. Reutter (quoted by Blum, *l.c.*) has found that they contain methylamine, dimethylamine and trimethylamine, as well as choline. Bourquelot and Hérissey (Compt. rend. 1900, **130**, 42, 731) have examined the carbohydrates of the seed. H. E. Wunschendorff (J. Pharm. Chim. 1919, [vii], **19**, 397) found that the seeds contain about 7% of a yellow oil, possessing a characteristic unpleasant taste. It does not solidify in the elaidin test, but dries rapidly on glass, forming a bright yellow skin, which is insoluble in ether. A sample gave the following analytical figures: d_{15}^{15} 0·9471; $n_D^{22\cdot5}$ 1·4774; acidity 3·20% as oleic acid; saponification value 189·5; iodine value 137·8; Hehner value 93·8, volatile fatty acids 1·5%; unsaponifiable matter 0·90%; lecithin 6·25%; phosphoric acid 0·55%. The fatty acids consisted chiefly of palmitic and linolic acids, with a smaller quantity of oleic and linolenic acids.

A. von Lingelsheim (Arch. Pharm. 1928, **266**, 218) states that the colouring matter of the seeds is found in the palisade layer of the testa and also in the tissues of the embryo. It is a flavone derivative and may be identified by the reaction of Willstätter and Everest. The whole seed is employed to avoid the extraction of the mucilage and is macerated for 24 hours in a moderate quantity of water to obtain a strongly tinted solution. A little magnesium-mercury amalgam is added to the filtered solution and, with constant shaking and cooling, small quantities of hydrochloric acid, resulting in the reduction of the flavone to a red-coloured derivative.

The Whole Plant.—According to analyses by D'Ancona (Landw. Versuchs-Stat. 1899, **51**, 387), the percentage composition of the dry matter is:

Protein.	Fat.	N-free extract.	Crude fibre.	Ash.
13·4	3·4	47·0	30·6	5·6

The percentage composition of the pure ash is:

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
19·1	7·6	29·8	1·0	4·9	8·1	4·1	23·5	1·1

In composition, fœnugreek resembles crimson clover and it is recommended as a farm crop. Since, however, the peculiar flavour of the plant is transmitted to both milk and meat, the fodder is more suited for working animals than for fattening or milk production. The peculiar odour and flavour of the plant is said to be due to the oil; it is very pronounced in the spring, but becomes less when the plant ripens.

T. McL.

FOLINERIN. A glycoside now known to be identical with *oleandrin* (*v.* Vol. II, 386*b*).

FOOD PRESERVATION is a subject discussed in several articles in this Dictionary, *e.g.* Food Preservatives, Fumigation, etc., and the present article will deal briefly with canning and gas storage of food.

Canning and Bottling.

The first large-scale success in bottling foods was due to Charles Appert (*v.* Bibliography) a French chef. His idea was to heat the food out of contact with air as access of air was considered to be the cause of putrefaction. Stout glass bottles nearly filled with food, already partly cooked, were carefully corked and heated in a water bath for times depending on the kind of food (Drummond and Wilbraham, "The Englishman's Food," p. 376). Canning food, however, rather than bottling, was destined to be a great industry, and this was started about 1813 by Bryan Donkin and John Hall of Dartford Iron Works, Kent, who first introduced tinned iron containers.

The canning industry prospered in Australia and the U.S.A. where there was surplus beef for canning and export to England as a cheap food (1866 onwards). The technical improvements necessary for the development of the huge American industry were stimulated by the demand for Army supplies during the American Civil War (Cruess, "Commercial Fruit and Vegetable Products," 2nd ed., McGraw-Hill Book Co., New York, 1938).

Cans.—Before 1903, the food was inserted through a circular opening in the top of the can, a disc or the lid itself, provided with a small vent hole, was soldered over the opening and after preliminary heating to displace air by steam this hole was sealed with a drop of solder, the can was then ready for processing. Among other objections to this "hole and cap" tin was the possibility of contaminating the food with traces of lead from the solder. The "hole and cap" can is handled twice, as there are two periods of heating in the sterilising retort (autoclave in other industries). Except for special purposes the sanitary or solderless can is now in general use. This can is not soldered on any inside joint, only the external side seam of the can body is soldered. The tinplate as purchased is usually coated with one or two coats of a stoved lacquer. The end pieces are stamped out of the same tinplate, flanged, and a rubber sealing composition is run into the flange. The bottom of the can is affixed in a double seaming machine (for details *v.* O. and T. W. Jones, "Canning Practice and Control," Chapman and Hall, London, 1937). The lid is attached by a similar machine after the filled can has been heated to expel air or after the air has been evacuated during the continuous flow of cans on the automatic can line. British Standard No. 866—1939, contains a schedule of sizes of metal containers for food products for British packers in the United Kingdom.

Tinplate.—Coating sheet iron with tin was a secret manufacture in Bohemia and Saxony. The process was brought to England in 1671 and a successful manufacture was started in Pontypool about 1720 by John Hanbury (Eaton, Food Manufacture, 1939, **14**, 48). The base metal of the tinplate was formerly wrought iron but is now steel. The unit quantity of tinplate is the base box containing 112 sheets coated with 0·85–3·25 lbs., total weight of tin per box, grades A to G each of 28–32 B.G., 14 × 20 in. of steel. (For glass containers *v.* Barnby, Food Res. 1938, **3**, 240; for substitutes for tinplate *v.* Williams, *ibid.* 278; *cf.* Hoare, Internat. Tin Research Council, Techn. Publications A. No. 30).

Corrosion of the steel by acid fruit juices liberates hydrogen which may exert a pressure sufficient to bulge the ends of the can, and discoloration of several kinds results from the solution of iron or tin. Traces of dissolved ferric iron combine with tannins, so that apples may be blackened especially after exposure of the fruit to air. A good vacuum in the tin is a preventive measure (Morris and Bryan, D.S.I.R. Food Invest. Special Rept. No. 40, 1931, p. 70). In a later report the same authors state that strawberries showed a marked discoloration in presence of 2 p.p.m. of iron, which with 5 p.p.m. was sufficient to condemn the fruit. Dissolved tin reacts with the soluble anthocyanin colouring matters; Sn, 2 p.p.m. gives a bluish shade to black currants, 10 p.p.m. would justify rejection (*ibid.* Special Rept. No. 44, 1936, p. 50, Second Rept. "Corrosion of the Tinplate Container"). It follows that all fruits containing anthocyanins should be packed in double-lacquered cans. The worst blackening is due to ferrous sulphide; the sulphur may be derived from the food, or from residues of sprays on fruit, or from ultramarine blue in the sugar added to the juice.

Traces of dissolved metals have a marked effect on the palatability of the canned food. The sense of taste is sufficiently sensitive to detect the following concentrations of metals in p.p.m. of orange juice: copper 20; ferrous iron 30–40; ferric iron, tin, aluminium, chromium, nickel, each about 100 (Tressler, Joslyn and Marsh, "Fruit and Vegetable Juices," AVI Publishing Co., New York, 1939). It is generally believed that even smaller traces of copper and iron catalyse oxidation reactions resulting in an "off-flavour" and darkening (Shrader and Johnson, Ind. Eng. Chem. 1934, **26**, 869; Joslyn and Marsh, Food Ind. 1933, **5**, 172; for non-corrodible equipment *v.* Bitting, Food Res. 1938, **3**, 245).

Both tin and iron may dissolve in canned fruit or vegetable juices. Adam and Horner (J.S.C.I. 1937, **56**, 329T) found **Sn**, 10–40 p.p.m. in fruit in lacquered cans after one year's storage at ordinary temperature; in plain cans **Sn** varied from 40 to 100 p.p.m. They found that iron rarely exceeded 10 p.p.m. and was generally little more than a trace. The maximum tin content permissible in Great Britain is 2 gr. per lb.=285 p.p.m. originally proposed by Buchanan and Schryver. Dissolved tin is greatly increased when the open tin of food is exposed to the air for several days. Tin is a normal constituent of animal organs, Bertrand and Ciurea found 0·4–26 p.p.m. (Compt. rend. 1931, **192**, 780).

Hydrogen swells is the term describing the condition of cans the ends of which bulge from the internal pressure of hydrogen evolved from the reaction of the metal with the acids of the food-stuff, notably fruit and vegetable. On prolonged storage the majority of cans show this defect. The early stages are known as "springers" or "flippers," the last stage is perforation or a "blow," rarely the pressure may burst the can. One means of postponing the condition is a good vacuum in the can.

Swells are sometimes the consequence of inadequate processing as regards time or temperature. Kidney (Food, 1937, **6**, 312, 322) observes that the gases in blown cans of meat are usually CO_2, N_2 and traces of O_2, if hydrogen is absent the tinplate has not corroded appreciably.

It was found that tin is anodic to the steel base (Adam and Horner, *l.c.*, 330T) but as the corrosion continues the polarity may be reversed (Hoar, Trans. Faraday Soc. 1934, **30**, 472). Lacquering actually tends to favour perforation for the corrosion of steel going on through pores in the lacquer and tin surfaces is a localised effect (Culpepper and Caldwell, J. Agric. Res. 1925, **35**, 107; Amer. Chem. Abstr. 1927, 3991). The lacquer coating, however, is necessary to protect the tin and prevent discoloration.

W. B. Adam (Chem. and Ind. 1938, **16**, 682) discusses the theory of the tin-iron couple in corrosion (Lueck and Blair, Trans. Electrochem. Soc. 1928, **54**, 257; Hoar, *l.c.*, and Amer. Chem. Abstr. 1939, 8549, 9245; 1940, 2482). Morris (J.S.C.I. 1935, **54**, 6T) states that the efficiency of gelatin as an inhibitor of corrosion depends on p_H; its effect was negligible at p_H 5·5 but very marked in a medium as acid as 2·4. The protection of the tin surface may be improved by lacquering the can after fabrication, and the method described in B.P. 455810 is a practical one (Clayton) (Food Manufacture, 1937, **12**, 119).

Canning Operations.—The preliminary process for successful food canning is the selection, cleaning and grading of the raw material—fruit, vegetables, meat, fish, etc. In mass production the cans are moved mechanically through all the following processes: (*a*) The food stuff is packed into open cans which are next filled to a prescribed level or weight with syrup for fruits, brine for vegetables, jelly for meats, oil or tomato sauce for fish. (*b*) The lids are lightly clinched on the cans but not so as to make a perfect joint, and air is displaced from the cans by the steam of a pre-cooking operation in the case of cans of fruit or vegetables which are conveyed through an exhaust box containing water at about 200°F., the time of immersion being about 5 minutes. The air imprisoned in the tissues of the food and contained in the headspace of the can is displaced, the lid is then fastened down by a double seaming machine. Tins of meat are exhausted of air in a vacuum chamber and the lids fastened down by a double seaming machine without breaking the vacuum, this process is carried out without heating. The soldered vent hole method is also in use. (*c*) The cans thus hermetically sealed and with concave ends owing to the internal vacuum are processed (sterilised) in a continuously working cooker or retort. An acid reaction is favourable to sterilisation, for example acid fruits may be processed at 200° F. for 10 minutes, the less acid vegetables at 240–260°F. for 20–45 minutes, while meat is cooked for hours, often in 2 or 3 stages of increasing temperatures. Retorts have been designed with steam-tight doors so that the continuous movement of the cans is not interrupted by shutting off steam to remove the cans. (F. H. Woodcock and W. R. Lewis, "Canned Foods," Pitman & Sons, London, 1938; Internat. Tin Research Development Council Inf. Circ. No. 1, 1937). (*d*) Cooling with jets of water or in a current of water or cold air follows immediately on the process of sterilisation (Crosbie-Walsh, Food Manufacture, 1938, **13**, 232; Morris and Bryan, *l.c.*, Special Rept. No. 40, p. 77).

A shorter process, flash pasteurisation, is possible with acid fruit juices (Cruess, J.S.C.I. 1939, **58**, 773; Charley and Harrison, *v.* Bibliography). Citrus juice is de-aerated under a high vacuum and passed through a heating coil in which it is heated to 90–95°C. for 1 minute, cooled to about 80°, canned and sealed while hot, then cooled as rapidly as possible. The high temperature is necessary to destroy heat-resistant enzymes (Cruess, *l.c.*). A similar method is in use for apple juice, which is centrifuged, treated with an enzyme to destroy starch, filtered, de-aerated under a vacuum of 29 in. then heated to 185°F. for 20 seconds. The temperature is reduced to 140° by passage through a cooler and the juice is then filled into cans and sealed (T. W. Jones *v.i.*). For the composition of the gases evacuated from fruit juices *v.* Pulley and Von Loesecke, Ind. Eng. Chem. 1939, **31**, 1275.

Processing (sterilisation).—The times and temperatures of processing must be so related that the finished product does not contain living micro-organisms or their spores (T. W. Jones, J.S.C.I. preprint 12/4/1940; O. Jones, Food, 1937, **6**, 300; Bigelow, *v.* Bibliography). Parallel with investigations of the thermal death-times of bacteria have been measurements of the rate of transfer of heat from the heating water or steam to the *centre* of the can, and the effect of the p_H of the juice, an acid reaction assisting sterilisation. Ball has published a graphical method of calculating the correct time and temperature of processing from these data (Canner, 1927, **64**, 27). Nelson and Berrigan (J. Agric. Res. 1939, **59**, 465) consider that complete sterilisation is seldom obtained in canning meats, although no organism may grow for a reasonable time of storage. They found that test organisms in a No. 2 meat can were usually killed by 65 minutes exposure to 15 lb. steam pressure (121°C.). The test organisms included *B. Coli*, *C. botulinum* and *Salmonella* types (*cf.* Savage, *infra*). A recent development has been heating for a shorter time to a higher temperature than usual, a method studied especially by Ball (Food Res., 1938, **3**, 37; *v.* pp. 49–55 for bibliography and patents).

Correct processing of meat and fish destroys the specific bacteria and toxins associated with food poisoning. Researches by Savage and others dispelled the popular idea that tainted meat (although objectionable) necessarily caused food poisoning (W. G. Savage, "Canned Foods in Relation to Health," Cambridge University Press, 1923; Lancet, 1939, ii, 991; S. Dixon, "Relation of Food to Disease," Inst. Chem. Lecture, 1932; Burnford, Brit. Med. J. 1938, i, 620).

Metallic Contamination.—Canned food has been known to contain metallic salts in objectionable amount, although traces, believed harmless, are common. There is an extensive and increasing literature of special and general methods for detecting and estimating the metals likely to occur in food. The Bibliography, 1921–33, of the Society of Public Analysts should first be mentioned, and on the experimental side the collaborative work and the investigations of individual referees of the Association of Official Agricultural Chemists which appear annually in recent years. The reports are prefaced by a separate discussion by Wichmann and thus may be readily found in the Journal of the Association and in the abstract Journals. In 1938 and 1939 the methods examined were for **As, Cu, Zn, (F) Pb, Hg, Se.** Bibliographies of single metals are contained in G. W. Monier-Williams' reports on analytical methods published by the Ministry of Health. For metals in food colouring materials reference should be made to the Reports of the Sub-Committee of the Society of Public Analysts (*e.g.* Macara *et al.*, 3rd Rept. Analyst, 1939, **64**, 339). The detection of metals is treated in the manuals of Food Analysis by H. E. Cox and other authors (*v.* Food Preservatives). Mention may be made of the chapter on metals in food in M. B. Jacobs' "Chemical Analysis of Foods," D. Van Nostrand Co., New York, 1938, pp. 120–143. Spectroscopy has been applied to this branch of analysis by Drea for milk (J. Nutrition, 1934, **8**, 229; 1938, **16**, 325) and by Harrison (Food Res. 1938, **3**, 121).

The following references to articles in this Dictionary and to recent papers in the literature may be cited:

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Aluminium.—Monier-Williams, Min. Health, Rept. Public Health Med. Subjects, No. 78, 1935. Lampitt *et al.*, Analyst, 1932, **57**, 418; Lunde, J.S.C. I, 1937, **56**, 334 T. *See also* Vol. II, 592, 650; volumetric, Vol. II, 650; colorimetric, Vol. II, 669; spot test, Vol. II, 579.

Copper.—Wichmann, *l.c.* Drabkin, Amer. Chem. Abstr. 1939, **33**, 6969. In tomato products: Sage and Stevens, Analyst, 1938, **63**, 719. Microchemical: Bertrand and L. de Saint-Rat, Mikrochim Acta, 1937, 1, 5. *cf.* von der Heide and Hennig, Z. Unters. Lebensm. 1933, **66**, 341; spot test, Vol. II, 580. Lampitt *et al.*, Analyst, 1935, **60**, 376. *See also* Vol. II, 586; volumetric, Vol. II, 656; electrolytic, Vol. II, 700; colorimetric, Vol. II, 671.

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GAS STORAGE.

Gas storage is the comparatively recent art of preserving and treating foodstuffs, while in storage or transit, by maintaining an atmosphere of controlled composition, temperature and often also of regulated relative humidity. The effect of keeping the foodstuff in the artificial atmosphere may be (*a*) to prevent or retard spoilage, especially that caused by micro-organisms or by an unsuitable humidity, (*b*) intentionally to accelerate or retard the ripening of fruit and other foods. Gas storage is to be distinguished from FUMIGATION (*q.v.*), a process in which the food is kept for a relatively short time in an atmosphere rendered sufficiently toxic to act as an insecticide, by the addition of ethylene oxide, carbon disulphide, sulphur dioxide, etc.

Storage in conditioned air is not regarded as gas storage, for air conditioning affects only temperature and relative humidity. In gas storage, temperature and relative humidity may be controlled but the characteristic feature is an artificial atmosphere of nitrogen, oxygen and carbon dioxide in proportions which differ widely from those in ordinary air, and the object achieved is delayed ripening, in effect the life of the fruit is prolonged. In another branch of the art the atmosphere in the store is altered by addition of a trace of an active gas such as ethylene for the purpose of accelerating the ripening of fruits, or by adding traces of ozone for preventing the growth of moulds.

Water Vapour may be regarded as a gas requiring control in food storage rooms as shown by the following instance, Culpepper and Caldwell (B. 1928, 241) stored dried apples at 20–30° and varied the relative humidity between 0 and 100%. Above relative humidity 80·5% there was a rapid growth of fungus, between 80·5% and 47% there was no fungal growth but the fruit deteriorated and became unmarketable. At relative humidity 18·5% or less, evaporated apples preserved their quality indefinitely. Methods of humidity control belong to air conditioning, for which see special works.

Loss of weight and shrinkage of foods will take place in cold storage unless prevented by maintaining a sufficiently high relative humidity, unfortunately higher humidities promote a rapid growth of moulds and bacteria on meat, eggs, fruit and vegetables (*v.* Prescott and Proctor, "Food Technology," McGraw-Hill Book Co., New York, 1937).

Storage of Food-stuffs in Carbon Dioxide (*cf.* Vol. II, 326*b*).—Several early workers attempted to preserve food by displacing the contained air by an inert gas. Bethall in 1848 displaced the air dissolved in milk and cream by carbon dioxide (A. W. Blyth, "Foods," 3rd ed., 1888, p. 165). Later, Valley and Rettger (J. Bact. 1927, **14**, 101) tested the effect of CO_2 on milk and cream, the reduction in the count of bacteria was found to be negligible, the effect observed was due to increased p_H. The authors state that removal of CO_2 from an environment otherwise favourable to development results in complete cessation of bacterial growth, even anærobic organisms appear to require CO_2 for continued existence (*v* Vol. IV, 23*a*). The successful use of CO_2 in the storage of food is based on the addition of regulated amounts of CO_2 for retarding the rate of ripening during transport and storage. Fruit and vegetables evolve CO_2 in the respiration of the cells, *e.g.* Benoy (B. 1929, 736) found that the CO_2 expired from green vegetables corresponded to oxidation of dextrose. In an atmosphere of CO_2 the respiration of unripe apples is retarded and the hydrolysis of protopectin to soluble pectin which is characteristic of ripening is inhibited. Spoilage of fruit and vegetables during transit is readily prevented by CO_2 gas-storage, but a consequent deterioration of flavour sets a limit to the method (U.S. Dept. Agric. Techn. Bull. No. 318, 1932). Prolonged researches have been carried out by the Food Investigation Board on the storage of fruit in atmospheres differing widely in their content of CO_2, O_2 and N_2 (*v.* Bibliography for summarised account) and the conditions for CO_2 gas-storage have now been established. Attention should be called to N. C. Thornton's researches at the Boyce Thompson Institute, Yonkers U.S.A. (*v.* Bibliography). A low percentage of CO_2 retarded respiration and ripening and reduced astringency and acidity; high percentages of CO_2 impaired the flavour of all the fruit and vegetables tested. The span and speed of life in fruits can now be controlled by storage in an atmosphere containing a suitable proportion of CO_2 which may be derived from the fruit itself, ripening is thus retarded and the life of the fruit lengthened, similar effects are produced by the use of atmospheres containing much less oxygen than air. F. Kidd (Proc. Roy. Inst. 1935, **28**, 351) showed that the vapour given off from ripe apples produced the same effects on seedlings and on unripe apples as air containing ethylene. The apples showed an immediate increase in respiration followed by development of odour, flavour and colour. The literature of this subject and of the treatment of food with ozone is summarised in the bibliography.

Bibliographical Summary.

Since recent literature on gas storage is far too extensive to report in this article, the following summary of references has been compiled to indicate briefly the contents of the publications or the conclusions reached by their authors.

Atmospheres Enriched with Carbon Dioxide.—(I) *Storage of Eggs.*—R. B. Haines, "The Storage of Eggs," D.S.I.R. Food Invest. Spec. Rept. No. 26, H.M. Stationery Office, London, 1926 (includes measurement of humidity, pp. 7–14); "Microbiology in the Preservation of the Hen's Egg," *ibid.* Spec. Rept. No. 47, 1939; "Preservation and Storage of Eggs," Chem. and Ind. 1940, **59**, 313, 394. T. Moran, J.S.C.I. 1937, **56**, 96T. T. Swenson, "Storage of Shell Eggs," Bull. Hygiene, 1939, **14**, 499; Food Res. 1938, **3**, 599. F. Kidd (B.P. 397848) uses absorbents of CO_2 to control the composition of the storage atmosphere.

(II) *Storage of Meat and Fish.*—R. B. Haines, "Microbiology in the Preservation of Animal Tissues," D.S.I.R. Food Invest. Specl. Rept. No. 45, H.M. Stationery Office, London, 1937. Pennington (Ice and Refrig. 1939, **96**, 235) stored meat for 35 days at 29–30°F. in 8–10% CO_2, the colour was preserved and the development of moulds and of rancidity prevented. Kaess, Angew. Chem. 1939, **52**, 17, a review with references. T. Moran (J.S.C.I. 1935, **54**, 151T) describes meat storage. Moran, Smith and Tomkins (*ibid.* 1932, **51**, 114T) found that CO_2 inhibited mould growth on meat especially at low temperatures. Callow (*ibid.* 116T), observed a similar effect on pork and bacon. Coyne (*ibid.* 119T; 1933, **52**, 19T) employed 50% CO_2 at 0° for preserving fish and inhibiting bacterial growth. Haines (*ibid.* 13T) compared the inhibiting effect of 10% and 20% CO_2. Killeffer (Ind. Eng. Chem. 1930, **22**, 140) found that CO_2 was absorbed in the surface layer of meat and fish, lowering the p_H and preventing bacterial growth. Fisk (Food Ind. 1936, **8**, 390, 446, 488, 571, 602) reviews the storage of meat in CO_2 and states that 10–20% is often more effective than higher concentrations.

(III) *Milk and Butter.*—Alekseev *et al.* (Amer. Chem. Abstr. 1936, 4935) preserved milk and butter in CO_2 but reported an acid flavour. Kidd and Moran (*ibid.* 1938, **32**, 7593) state that fats become rancid and fruit and vegetables brown in atmospheres enriched with CO_2, the remedy would be almost entire exclusion of O_2; storage in pure N_2 at 0° doubled the keeping quality of butter.

Margarine.—Lundsgaard (B.P. 468810) claims that CO_2 improves the keeping qualities.

(IV) *Storage of Fruit and Vegetables.*—C. Brooks *et al.* (U.S. Dept. Agric. Tech. Bull. No. 318, 1932; No. 519, 1936) found the rotting of fruit and vegetables was retarded in atmospheres containing 25% or more of CO_2 but a deterioration of flavour limited the time of storage. Zagoryanskiĭ (Amer. Chem. Abstr. 1934, 1417) observed that CO_2 from the respiration of the fruit accumulates under the paper wrappings in concentrations sufficient to inhibit mould growth at 0°. V. H. Blackman (Science Progress, 1939, **33**, 417) gives a review of fruit storage. Allen and Smock (Amer. Chem. Abstr. 1938, 7152) stored fruit in atmospheres containing 5–10% CO_2 and 6–11% O_2, the production of soluble pectin in the fruit was retarded and the period of marketability prolonged. Thornton (*ibid.* 7152) determined the effect of CO_2 storage on the vitamin C contents of some unripe fruits (diminished) and of ripe fruits (no loss). Eaves (*ibid.* 1939, **33**, 255) found usually an increase in p_H in the juice of fruits which had been stored in CO_2. High concentrations, 53·5%, of CO_2 depressed and low concentrations 6·25% stimulated the CO_2 output of fruits during storage for 5 days. Fungal invasion was retarded.

According to U.S.P. 1798781, fruit and vegetables are placed in storage in an atmosphere of 40% CO_2 diminished to 15% as the temperature falls.

(V) *Strawberries.*—Smith (D.S.I.R. Food Invest. Bd. Rept. 1937, 165) recommends an atmosphere containing 10% CO_2 and 10% O_2 maintained at 0°.

(VI) *Peaches.*—Tindale *et al.* (Amer. Chem. Abstr. 1939, **33**, 1828) stored peaches in 8–10% CO_2 without improvement as regards fungal decay.

(VII) *Bartlett Pears.*—Gerhardt and Ezell (B. 1938, 842) gave the pears a preliminary storage in 20–35% CO_2, the loss by surface scald was reduced.

(VIII) *Pears.*—Kidd and West (D.S.I.R. Food Invest. Bd. Rept. 1937, 93, 101) state that pears ripen when stored at 60–70°F. in an atmosphere containing 2·5% O_2 and 10% CO_2.

(IX) *Potatoes.*—Štastný (Amer. Chem. Abstr. 1939, **33**, 6466) found that potatoes deteriorated when stored in CO_2, they lost much starch and many rotted, controls in air were satisfactory.

(X) *Storage of Apples.*—Kidd and West ("Gas Storage of Fruit," D.S.I.R. Food Invest. Spec. Rept. No. 30, 1927) studied the respiration of apples in CO_2 atmospheres; and Food Invest. Bd. Rept. 1924–5–6, examined the chemical changes during senescence and observed that the rate of respiration of apples was halved and the length of storage life doubled by storing in an atmosphere containing 79% N_2, 12% CO_2 and 9% O_2. F. Kidd, C. West and M. N. Kidd (*ibid.* Spec. Rept. No. 30, 1927; J. Pomology, 1930, **8**, 67) find the optimum atmosphere for apple storage contains 10–15% CO_2 and 5–15% O_2 and is kept at 4–5°C. The results are 50% better than ordinary cold storage. Kidd and West (Hort. Education Assoc. Yearbook, 1933, 2, 59), record the optimal atmosphere and temperature for storing 12 named varieties of apples, also J. Pomology, 1933, **11**, 149. The same authors (Ice and Cold Storage, 1935, **38**, 169, 200) arranged for the CO_2 to be supplied by the respiration of the apples, so that the cold storage atmosphere contained 5% CO_2 and 5% O_2 and its composition was controlled by ventilation; in J. Pomology, 1936, **14**, 276, they describe the storage of Cox's Orange Pippins at 3·9° in an atmosphere containing 2·5% O_2 and 5% CO_2, an absorbent for CO_2 was provided; in Sci. Hort. 1936, **4**, 75, they state that the suitable concentrations of CO_2 vary with the variety and condition of the apples, harmful concentrations are unlikely below 4–5% CO_2 at a temperature of 34–36° F. In J. Pomology, 1937, **14**, 299, Kidd and West describe the construction of refrigerated gas-storage chambers, gas analysis apparatus and methods of control.

Ethylene.—As shown by the following references traces of ethylene (and of other unsaturated hydrocarbons) in the air of fruit storages accelerate ripening, moreover apples ripening in ordinary air evolve traces of ethylene.

Bananas.—Wolfe (Bot. Gaz. 1931, **92**, 337) accelerated slightly the yellowing of bananas by storage in air containing 1:1000–1:10,000 of ethylene. Quasi-dormant bananas commenced ripening immediately after treatment. Regeimbal *et al.* (Amer. Chem. Abstr. 1928, 4153) observed increased respiration and sugar production in air containing ethylene 1:1000. Gane (D.S.I.R. Food Invest. Bd. Rept. 1934, 122) detected C_2H_4 by biological tests in air which had been aspirated over apples, in this air bananas ripened and *Mimosa pudica*, which is sensitive to C_2H_4 at 0·1–8 p.p.m., showed effects characteristic of C_2H_4. Zavanaju (Amer. Chem. Abstr. 1937, 5470) found that air enriched with 50% O_2 was less effective than 100% C_2H_4 or C_2H_2 in ripening bananas and tomatoes. Bananas exposed to C_2H_4 for 11 days contained 13·82% sugar, the controls 4·52%. Commercial ethylene containing CH_4 30, C_2H_6 13, H_2 5, C_3H_6 2·5, C_2H_2 2·3% was much more efficient than pure C_2H_4, but the active constituent has not been recognised. Lynch (*ibid.* 1937, **31**, 2258) suggests that C_2H_4 acts as a co-enzyme to the oxidases in the banana and apple in both natural and artificially accelerated ripening.

Oranges and Citrus Fruits.—Ramsay and Musso (*ibid.* 1930, **24**, 5390), in experiments on colouring oranges with ethylene, found the total sugar content and the sugar/acid ratio were not altered, but 18% of the original sucrose was converted into fructose. Winston (*ibid.* 1934, **28**, 4799) observed that decay of citrus fruits coloured with C_2H_4 was caused by CO_2, 3–5%, accumulated in the colouring rooms. Fruit treated with C_2H_4 coloured as quickly and kept as well as fruit coloured by fumes from a kerosene stove. Winston and Tilden (*ibid.* 1935, **29**, 243) coloured oranges by treatment with ethylene in air of 85–92% relative humidity at 80–85°F. and confirm that CO_2 should not be allowed to accumulate in the colouring room. Winston (*ibid.* 8163) found that acetylene at the same concentration coloured citrus fruit less rapidly than C_2H_4, acetylene gave a relative improvement in keeping quality and freedom from scald, but treatment with either gas impaired keeping quality. Egaña and Acerete (*ibid.* 1936, 5671) advise treating oranges for 4 days with air of relative humidity 75–80% containing 0·2% C_2H_4 at 18–20°, renewing the atmosphere every 8 hours.

Tomatoes.—Kohmann (Ind. Eng. Chem. 1931, **23**, 1112) observed the reddening of green tomatoes stored for 5 days in air containing ethylene 1:5000. Zavanaju (*l.c.*) coloured tomatoes with ethylene, 0·2% showed little improvement over 0·1%.

Apples and Pears.—Science Library Bibliography No. 129, 1934, "Gas Storage of Apples." Ethylene is evolved from ripening apples, Gane (*l.c.*). Kamenický (Amer. Chem. Abstr. 1937, **31**, 5889) ripened apples and pears with dilute C_2H_4 at 18–20°, there was no effect from C_2H_4 below 16°. The treated fruit acquired a petroleum flavour and was more liable to spoil in air than the untreated fruit. Christensen *et al.* (Science, 1939, **89**, 319) describe a microchemical determination of the ethylene evolved from ripening apples. On the sixth day of storage at 65°F. Gravenstein apples yielded 0·2 ml. ethylene per kilogram-hour.

Yeast.—Nord and Franke (J. Biol. Chem. 1928, **79**, 27) found that ethylene stimulated enzyme action and that yeast suspensions treated with C_2H_4 fermented glucose more rapidly.

Plant Growth.—Zimmerman and Hitchcock (Amer. Chem. Abstr. 1933, 5780) found the growth of willow roots was stimulated by acetylene, ethylene or propylene.

Ozone.—Heiling and Scupin (*ibid.* 1937, 5401). Fungal growth on fruit in cold storage is considerably reduced in air containing ozone, bacteria were not affected to the same extent. Gane (D.S.I.R. Food Invest. Bd. Rept. 1935, 97), O_3, 2–3 p.p.m. did not injure some varieties of pears and apples in storage at 5° for 17 days, 40 p.p.m. did not damage oranges. C. H. Lea (*ibid.* Rept. 1936, 25), beef fat and lard become rancid if treated for 5 hours with air containing 5 p.p.m. O_3, no rancidity developed in the same fats kept in air for 4 months. Ewell (Food Res. 1938, **3**, 101), O_3, a few p.p.m., is useful in the cold storage of eggs and meat, fatty foods become rancid rapidly at O_3 concentrations which inhibit bacterial growth on food surfaces containing much H_2O. E. W. Riesbeck, "Air Conditioning," 2nd ed., Goodheart-Willcox Co., includes ozonising. B. Waeser (Chem. Fabrik, 1939, 129), bibliography includes ozone. W. H. Cook (Ice and Cold Storage, 1939, **42**, 8) reviews cold storage of fruits and meat in ozonised air. Scupin (Amer. Chem. Abstr. 1939, 1054), states that ozone treatment largely inhibited fungal and bacterial growth on food-stuffs. Kaess (Angew. Chem. 1939, **52**, 17), a review of ozone treatment.

J. N. G.

FOOD PRESERVATIVES.—In Murray's New English Dictionary, a preservative is a "chemical substance or preparation used to preserve things subject to decomposition as perishable food-stuffs"; the earliest quotation is, "Salt is not an effectual preservative," C. Lucas, Ess. Waters, 1756, II, 36; and the latest is from the "Westminster Gazette," 3/2, 23 February, 1898, "a question of great difficulty to the public analyst is the introduction of preservatives into articles of food."

In the Public Health (Preservatives, etc., in Food) Regulations, 1925 to 1939, Article 2 (1), "preservative" means "any substance which is capable of inhibiting, retarding or arresting the process of fermentation, acidification or other decomposition of food or of masking any of the evidences of putrefaction; but does not include common salt (sodium chloride), saltpetre (sodium or potassium nitrate), sugars, lactic acid, acetic acid or vinegar, glycerine, alcohol or potable spirits, herbs, hop extract, spices and essential oils used for flavouring purposes or any substance added to food by the process of curing known as smoking."

The decompositions and putrefaction abovementioned are known from the work of Pasteur (1822–95) to be associated with the rapid multiplication of micro-organisms, *i.e.* bacteria, moulds and yeasts[1] in the foods or beverages—micro-organisms which may have been present in the raw materials or may have infected the food-stuff at any or all stages from preparation to consumption. Since bacteria or their spores are usually abundant in air, water, dust, soil and on the hands of workers, almost all food-stuffs contain living bacteria unless special precautions are taken to exclude them. However, the bacteria will not multiply in or on a suitable medium such as a food-stuff unless certain conditions are satisfied as regards moisture, temperature, p_H, concentration of the products of their metabolism and the absence beyond small concentrations of antiseptics or preservatives (*v.* DISINFECTANTS). A great part of the mechanism of the degradation of food-stuffs is operated by the enzymes (*q.v.*) secreted by the cells, enzymes which attack specific components of the foods; the classical instance is yeast *zymase* (Buchner, Ber. 1897, **30**, 117, 1110) which ferments sugar. The rates of growth (multiplication) of different species of bacteria and the velocity of action of different enzymes severally on their respective substrates are retarded by chilling or freezing, by varying the p_H from the individual optimum or by adding preservatives or enzyme poisons. Bleyer *et al.* (Arch. Pharm. 1933, **271**, 539) studied the separate effects of 15 preservatives on 7 common enzymes. By heating above certain minimum temperatures, 100° is often sufficient, or by increasing the concentration of preservative both bacteria and enzymes are destroyed. For precautions necessary for resistant bacteria and spores, *see* Medical Research Council, "A System of Bacteriology," Vols. I and IX, H.M. Stationery Office, London, 1929–31. An early experimenter on these lines was D. Papin who used steam at 7 atmospheres pressure for preserving meat, bones, etc. ("A New Digester or Engine for Softening Bones," London, 1681).

Bacterial Spoilage.—Haines (Proc. Brit. Assoc. Refrig. 1936–37, **33**, No. 1, 134) has classified the kinds of spoilage caused by micro-organisms, tables of spoiled foods and of the causative bacteria are given.

Preserving Food.—The modern methods of preserving food by cold storage and transport, canning, etc., depend on a knowledge of bacteriology, but the empirical arts of preserving food are of great antiquity. The earliest methods were (I) drying, in the sun or by artificial heat, or (II) curing in wood-smoke, (III) pickling in strong brine, or nitre, (IV) in vinegar or alcohol, (V) heating and covering with syrup, (VI) or with butter, olive oil or spices. (VII) Packing in ice, (VIII) or charcoal (J. Sinclair, "Code of Health and Longevity," 1807, I, 431). Roman soldiers received a ration of salt pork, or a payment *salarium* = salt money (hence salary). Processes I, III and V depend largely for their success on the difference in osmotic pressure between the contents of the bacterial cells and the concentrated solutions in contact with them. Water passes outwards through the cell wall into the solution of high osmotic pressure and the cells are damaged or killed (*plasmolysis*). (For bacterial counts in dried foods, *see* Prescott, J. Bact. 1920, **5**, 109.) There are, however, species of micrococci which flourish in concentrated salt solutions (Pettersson, Arch. Hyg. 1900, **37**, 171; Macara, Proc. Roy. Inst. 1937, **39**, 657).

Wood Smoke.—Callow (Analyst, 1927, **52**, 391) found formaldehyde in wood smoke and in smoked ham. Pettet (D.S.I.R. Food Investigation Board Report, 1936, 111) estimated formaldehyde in wood smoke by Grützner's method (Arch. Pharm. 1896, **234**, 634) and total aldehydes and ketones by Parkinson and Wagner's iodometric method (Ind. Eng. Chem. [Anal.], 1934, **6**, 433). Pettet and Lane (Chem. and Ind. 1940, **59**, 258) found formaldehyde, acetaldehyde, furfuraldehyde, 5-methylfurfuraldehyde, acetone, diacetyl, methyl and ethyl alcohols, phenol, formic and acetic acids in the smoke.

The following authors studied the preservative action of wood smoke: Serafini *et al.* (Hyg. Rundschau, 1890, 267); Valagussa (Ann. d'ig. sperim. 1897, **7**, 546; Centr. Bakt. 1892, **11**, 577). Tillmans, "Handbuch der Lebensmittelchemie," Berlin, 1933, I, 1002, attributes the preservative effect mainly to surface drying but also to penetration to some extent of phenol, creosote (creosote (1835), by derivation is the meat preserver), pyroligneous acid, formaldehyde and other aldehydes. For further references, *see* Science Library Bibliography, "Smoke Curing," No. 427, 1938.

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[1] For convenience "bacteria" will include yeasts and moulds.

Vinegar usually contains 4% acetic acid (Vol. I, 46*d*), its preservative action in pickles is due mainly to the hydrogen-ion concentration (Norton and Hsu, J. Infect. Dis. 1916, **18**, 180; Taylor, Lancet, 1917, ii, 294) but it has a specific action on yeasts (Macara *l.c.* 677). The phenolic and aldehydic impurities in pyroligneous acid (crude acetic acid from wood distillation) are considered to confer advantages for preserving over synthetic vinegars (*cf.* Vol. I, 44*b*, 46*c*). Liverseege ("Foods and Drugs," 392, J. and A. Churchill, London, 1932) found that common moulds did not grow in vinegar (4% acetic acid) but that an organism, not named, grew and reduced the strength to 0·3% in 15 weeks. Vinegar eels have been studied by Peters (Analyst, 1928, **53**, 661). *Analysis.*—Uranylformate yields characteristic tetrahedra with 0·5 mg. acetic acid (Krüger and Tschirch, Mikrochem. 1929, **7**, 318). For the estimation of SO_2 in vinegar, *see* Vol. I, 47*d*; of formic acid, Vol. I, 53*c*.

Spices have been highly prized as preservatives from a remote past. Addition of spices to food not only masked the odour of putrefactive products, but also provided genuine antiseptics which arrested decay, although this was not recognised as lately as 1868 when it was still thought that a bad smell might cause an epidemic (Drummond and Wilbraham, "The Englishman's Food," pp. 35, 371, J. Cape, London, 1939). Corran and Edgar (J.S.C.I. 1933, **52**, 149T) tested the effects of various spices on fermentation by ordinary yeast. Mustard flour was the most efficacious, followed in order by cloves and cinnamon. Their volatile oils behaved similarly in the order: mustard, cinnamon, cloves, thyme and bay leaves. Many spices had little or no effect on fermentation. Mustard (0·5%) and mustard oil (0·02%) were definitely stronger than benzoic acid (0·06%) or sulphur dioxide (0·035%) while cloves spice was superior to sulphur dioxide and approximately equal to benzoic acid. The authors agree substantially with the majority of earlier workers quoted in the paper, excepting James (Food Ind. 1931, **3**, 524) who found cloves or cinnamon superior to mustard against *B. coli*. Fabian, Krehl and Little (Food Res. 1939, **4**, 269) state that ground cinnamon and cloves are the only spices active at low concentrations and are particularly effective against *Staph. aureus*. For the preservative action of essential oils, *see* Vol. IV, 30*d*; of peroxides in essential oils, *see* Bechhold, Z. Hyg. 1936–37, **119**, 193.

Hops have considerable preservative properties which are not diminished by removal of the volatile oils by steam distillation. Brown *et al.* (J. Inst. Brew. 1910, **16**, 641; 1913, **19**, 261) state that the inhibitive action of aqueous extract of hops on a bacterium culture is much stronger, weight for weight, than that of phenol, cupric sulphate or potassium metabisulphite. This method was standardised by A. C. Chapman (*ibid.* 1925, **31**, 13; 1929, **35**, 363; for colorimetric and gravimetric methods, *see* Walker and Parker, *ibid.* 1936, **42**, 267; *cf.* Applied Chem. Rept. 1926, **11**, 535). The method of determining the preservative value "(P.V.)" (*v.* Vol. II, 104*b*), is an estimation of the α- and β-resins. Hops may contain traces of sulphurous acid from the oast houses, but boiling removes or oxidises most of the SO_2.

Formaldehyde (*v.* Vol. IV, 26) as a food preservative was finally rejected by a majority of authorities on hygiene, although it was argued that in concentrations of formalin, 1:25,000 as used for preserving milk, the effect on health would be negligible (Tunnicliffe and Rosenheim J. Hyg. 1901, 1, 321; *cf.* Wiley, U.S. Dept of Agriculture Bureau of Chem. Report No. 5, 1908). Among those opposing the addition of formaldehyde to food were Buchanan and Schryver (Food Reports, No. 9, 1909, Local Government Board), who beside other arguments quote a testimonial received by a supplier of formalin "my bacon and cheese which were previously unfit for food are now saleable articles." Formalin was much used to retard the souring of milk (extensive literature, *i.a.* Richmond, Analyst, 1900, **25**, 122) until the Public Health (Milk and Cream) Regulations, 1912, prohibited the use of preservatives in milk. A preservative "*Mystin*" was sold for milk which was (wrongly) alleged to defy detection. It contained formaldehyde and sodium nitrite, the latter substance added with the object of defeating Hehner's Test (Monier-Williams, Local Government Board Food Report, No. 17, 1912; Analyst, 1912, **37**, 155, 178).

It was objected to formaldehyde that it damages the digestive enzymes especially trypsin, irritates the mucous membrane of the digestive tract and renders the proteins of serum insoluble (Schwarz, Z. physiol. Chem. 1901, **31**, 460). Further, while eliminating the odour of putrefaction it does not always destroy pathogenic organisms and acts only slowly on spores and toxins (Hailer, Biochem. Z. 1921, **125**, 69; Minett, J. Hyg. 1938, **38**, 623). Addition of 0·08% to milk was found to inhibit coagulation by rennet (Weitzel, Arb. Reichsgesundh. Amts. 1903, **19**, 164). Trillat found formaldehyde in freshly smoked meat (Rev. Hygiène, 1905, **27**, 148; *cf.* "Wood Smoke," *supra*). Hexamethylenetetramine also formerly used is a disinfectant in acid solution when it yields formaldehyde (Hanzlik and Collins, Arch. intern. Med. 1913, **12**, 578). Ice containing formaldehyde has been suggested as a preservative.

Detection.—*Phloroglucin reaction* according to Sabalitschka and Harnisch (Pharm. Zentralh. 1926, **67**, 289). Mix 2 c.c. of the test solution with a freshly prepared reagent consisting of 2 c.c. of 1% phloroglucin and 1 c.c. of 10% **KOH**; a characteristic fugitive red or pink colour which disappears in 12 minutes is given by dilute formaldehyde solutions. The colour fades gradually to yellow and then turns to blue-violet, the latter coloration is shown by the reagent alone on standing. Red colorations given by butyraldehyde and acetaldehyde last 4 and 6–8 minutes respectively, furfuraldehyde gives a permanent red colour (*cf.* Rosenthaler, *ibid.* 1932, **73**, 737).

Phenylhydrazine Reaction.—Rimini (Z. Unters. Nahr. Genussm. 1898, **1**, 858) mixed 15 c.c. of test solution with 1 c.c. aqueous 4% phenylhydrazine hydrochloride, and 3–4 drops of also freshly prepared 0·5% sodium nitroprusside solution, then made strongly alkaline with a few drops of conc. $NaOH$. A blue coloration is given by formaldehyde, limit 1 p.p.m. Acetaldehyde, furfurol, benzaldehyde, acetone and methyl alcohol do not react in this way, boric acid does not interfere. The mixed reagents alone give a red colour. Schryver's modification is more sensitive (Proc. Roy. Soc. 1910, B, **82**, 226). The reagents added to 10 c.c. of the test solution are: 2 c.c. of freshly prepared and filtered 1% phenylhydrazine hydrochloride, then 1 c.c. of fresh 5% potassium ferricyanide, finally 5 c.c. of conc. hydrochloric acid. A brilliant magenta colour indicates formaldehyde and its intensity gives an indication of the quantity present within the limits $1{:}10^5$ and $1{:}10^6$. Fincke's test (Z. Unters. Lebensm. 1914, **27**, 246) is carried out with a modified Schiff's reagent with which acetaldehyde gives only a fugitive colour, while furfuraldehyde does not interfere with the relatively permanent colour which develops in presence of formaldehyde. Denigès' method (Compt. rend. 1910, **150**, 529) is very similar and is operated by Elvove (Ind. Eng. Chem. 1917, **9**, 295) for colorimetric purposes with a reagent prepared from anhydrous sodium sulphite.

Dimedon (5:5-Dimethyldihydroresorcinol) *q.v.* precipitates formaldimedon crystals, m.p. 189°, even from 0·004% $HCHO$ solutions, a test suitable for microchemistry; with a solution containing 0·00005% $HCHO$, a distinct turbidity is visible after standing 4–6 hours (*cf.* Jonescu *et al.*, Bull. Soc. Chim. 1930, [iv], **47**, 1408). The corresponding acetaldimedon has m.p. 139° (Vorländer, Z. anal. Chem. 1929, **77**, 321).

Formaldehyde (*I*) *and Hexamethylenetetramine* (*II*) (R. Fischer, Z. Unters. Lebensm. 1934, **67**, 171).—The separation depends on the fact that II is not appreciably decomposed when an alkaline solution of (I) and (II) is cautiously warmed on the waterbath. The micro-beaker containing the solution is covered with a slide carrying a few crystals of dimedon in a suspended water drop, very fine needles (m.p. 189°) of formaldimedon are formed. The contents of the beaker are evaporated to dryness finally over H_2SO_4 *in vacuo*, 0·5 c.c. water added and the test for (I) with dimedon repeated, this should now be negative. The liquid is acidified with excess of H_2SO_4 and warmed when the test now gives a positive result from the (I) liberated. Finally the liquid is made alkaline and warmed beneath a slide carrying a drop of a suspension of dinitro-α-naphthol, the NH_3 formed in the decomposition of (II) reacts to form needles, m.p. 175° (Klein and Steiner, Jahrbücher wissensch. Botanik, 1928, **68**, 602). Sensitivity (I) $20\mu g.$; 1:100,000 with 2 c.c. solution; with 10 c.c. in a small flask, 1:250,000. For the technique, *see* R. Fischer, Archiv. Pharm. 1933, 271, 466; *cf.* Kollo and Polychroniade, Pharm. Zentralh. 1932, **73**, 578). (II) may be detected as the ferrocyanide, Behrens-Kley, "Organische Mikrochemische Analyse," 2nd ed. 1922, p. 67.

Hehner's (*Tryptophan*) *Reaction* (literature cited by H. Meyer, "Nachweis und Bestimmung organischer Verbindungen, Berlin, 1933, 47).—About 0·1% of peptone, casein or albumen or 2 c.c. fresh milk (free from aldehydes) is dissolved in 5 c.c. of the test solution, to this is added 7 c.c. of 25% HCL containing 0·02% ferric chloride, and the mixture gently boiled for about 30 seconds: formaldehyde gives a violet coloration (Leonard and Smith, Analyst, 1899, **24**, 86). Heimrod and Levene (Biochem. Z. 1910, **25**, 18) mix 1 c.c. of the original solution with 1 or 2 c.c. syrupy phosphoric acid (*d.* 1·7) 1 drop of a dilute solution of peptone (*v. supra*) in phosphoric acid followed by 1 drop of 5% $FeCl_3$ solution. Conc. H_2SO_4 is then poured below the cold solution, when a violet zone appears if aldehydes are present. If Hehner's reaction with the same specimen is negative, formaldehyde is absent, if both tests are positive another aldehyde may be present as well as formaldehyde.

Fluorides.—The manufacture or sale of any article of food containing any addition of fluorides is an offence under the Preservatives in Foods Regulations. The 1924 Report of the Departmental Committee considered fluorides to be among the most objectionable preservatives. They are also among the most effective: Gottbrecht found that hydrofluoric acid in 0·1% solution prevented putrefaction of meat (Ther. Monatsh. 1889, **3**, 411). Fluorides were formerly added to butter to prevent mould growth (Monier-Williams, "Food and the Consumer," Inst. Chem. Lecture, 1935, 5). Rost (14th Internat. Congr. Hyg. 1907, **4**, 166) reported that fluorides were cell poisons and and specifically harmful for the metabolism of bones and teeth. It was discovered in 1890 that cattle fed on the spent grains of German distilleries in which Effront's antiseptic for yeast, hydrofluoric acid, had been used, developed brittleness of the bones.

The Chief Medical Officer of the Ministry of Health (Annual Report, 1937) records that the presence of fluorine, 2–5 parts per million, in water supplies was sufficient to cause "mottled" teeth; he remarks that there is no evidence that fluorine even in the smallest amount is an essential constituent of bones or teeth (*cf.* Vol. II, 27*c*). T. von Fellenberg (Mitt. Lebensm. Hyg. 1937, **28**, 150) found 0·005% in milk teeth. As a result of this fluorine disease, better known in the United States than in England, the enamel becomes brown and may be destroyed. (A. 1937, 364, three references; Monier-Williams, *l.c.*; Ellis and Maynard, Amer. Chem. Abstr. 1937, 435). Phosphate fertilisers containing 3–4% F may cause contamination of well water. The use of barium fluosilicate and of cryolite sprays is suspect, since fruit may retain 3–6 parts F per million (Ministry of Health, *l.c.*). Griebel *et al.* (Z. Unters. Lebensm. 1938, **75**, 305) analysed apricot preserves which had been the cause of several outbreaks of fluorine poisoning.

Detection (Vol. II, 576*a*, 582*a*).—The colorimetric methods may be employed: lanthanum acetate detects 0·01 mg. F in 10 c.c. (Meyer and Schulz, Z. Angew. Chem. 1925, **38**, 203). Zirconium alizarinsulphonate is approximately as sensitive (de Boer, Chem. Weekblad, 1924, **21**, 404; Smith *et al.*, Ind. Eng. Chem. [Anal.], 1934, **6**, 61). Ulex (Chem.-Ztg. 1925, **49**, 845) employed the La method to detect F naturally present in egg yolk. The spectroscopy of the sensitive characteristic CaF_2 band (Ryde and Yates, Trans. Soc. Glass Tech. 1926, **10**, 274) should be mentioned. For spot tests, *see* Feigel, "Qualitative Analyse-Tüpfelreaktionen," 2nd ed. Leipzig, 1935, 283.

Determination (*v.* Vol. II, 607*c*, as $PbClF$; p. 673*b*, pertitanate, colorimetric).—Dan Dahle (J. Assoc. Off. Agric. Chem. 1937, **20**, 205; 1938, **21**, 208; 1939, **22**, 338) describes four methods of determining fluorine which have been studied collaboratively: (*a*) peroxidised titanic salt, (*b*) and (*c*) thorium nitrate titration, (*d*) Armstrong's microtitration. None of these methods have given complete satisfaction (1939) for small proportions of F. T. von Fellenberg (*l.c.*) found about 0·3 mg. F per litre in wine, employing Willard and Winter's thorium nitrate method (Ind. Eng. Chem. [Anal.], 1933, **5**, 7; Winter, J. Assoc. Off. Agric. Chem. 1936, **19**, 362). Lockwood (Analyst, 1937, **62**, 775) modified the method to avoid a serious error in presence of Mn. Griebel *et al.* (*l.c.*) claim to avoid distillation by ashing with CaO and $Cu(OAc)_2$ in a known modification of the zirconium method (*cf.* 3 references A. 1934, 500). McClure ("Fluorides in Food and Drinking Water," Nat. Institute Health, Bull. No. 172, Washington 1939) prefers Armstrong's micro method (Ind. Eng. Chem. [Anal.], 1936, **8**, 384) incorporating the distillation described by Hoskins and Ferris (*ibid.* 6). In the U.S., sprayed fruit must not contain more than 2·8 p.p.m. of F (*cf.* Ministry of Health, *supra*).

Nitrates and Nitrites.—Nitrates are not classed as preservatives in the Public Health (Preservatives, etc., in Food) Regulations, 1925 to 1927, and by Provisional Regulations, October 20, 1939, sodium or potassium nitrite is permitted in bacon, ham and cooked pickled meat. The nitrites mentioned may not exceed 200 parts per million (as $NaNO_2$) in cooked pickled meat, there is no limit stated for bacon or ham. Although the experimental animals showed no obvious effects an opinion adverse to nitrites (in flour) was formerly adopted (Food Inspectors' Reports, No. 12, 1911, Cd. 5613). The maximum now specified, 1·4 grains per lb., may be compared with the medicinal dose ½–2 grains (B.P.C. 1934).

The permission is of interest in connection with researches carried out by the Food Investigation Board on the denitrifying organisms in the bacon pickle, strong brine containing additions of potassium nitrate and sugar (*cf.* Horowitz-Vlassova, Z. Unters. Lebensm. 1931, **62**, 596). The majority of the organisms in the pickle are micrococci capable of growth in media containing as much as 20% $NaCl$ (*halophiles*), some varieties of these reduce nitrate to nitrite (Macara, Proc. Roy. Inst. 1937, **29**, 676). In investigating these bacilli it was found that glucose was oxidised at the same time that nitrate was reduced (D.S.I.R. Food Investig. Bd. Rept. 1935, 8). Nitrite reacts with the hæmoglobin of the bacon producing in the absence of oxygen nitroso-hæmoglobin with the characteristic pink colour. The brown discoloration seen on the surface of bacon is methæmoglobin formed when oxygen is present. The reaction has been investigated by J. Brooks (Proc. Roy. Soc. 1937, B, **123**, 368).

Analytical (qualitative, Vol. II, 572*c*; colorimetric, Vol. II, 673*c*).—The determination of nitrite in presence of nitrate was carried out by the method of Baumgarten and Marggraff (Ber. 1930, **63** [B], 1019) who measured the nitrogen evolved in the reaction,

$$NaNO_2+NH_2SO_3H=NaHSO_4+H_2O+N_2.$$

Lutzenko (J. Appl. Chem. Russ. 1937, **10**, 948) applied the amidosulphonic reagent to the analysis of curing pickles, and washed the nitrogen with KOH to remove CO_2 and SO_2 before measurement. J. Brooks and J. Pace have devised a delicate manometer for use with small quantities (D.S.I.R. Food Investig. Bd. Rept. 1938, 77). Iodometric titration in a CO_2 atmosphere with or without addition of urea (Vetror, J. Applied Chem. C.S.S.R. 1936, **9**, 1363 (in English)) has no apparent advantages.

W. Plücker (Z. Unters. Lebensm. 1934, **68**, 187) recommends two methods for determining nitrite in pickling salt, *i.e.* in presence of sulphite, nitrate and sugar (sucrose): (*a*) Grossmann-Peltzer's method depends on the reaction,

$$3NaNO_2+H_2SO_4 \\ =Na_2SO_4+NaNO_3+2NO+H_2O;$$

10 g. of the sample are dissolved in 150 c.c. of water and neutralised to phenolphthalein, 15 c.c. of $N/10$ H_2SO_4 are then added, the mixture is boiled to expel nitrous fumes, cooled and titrated back with $N/10$ $NaOH$ (Chem.-Ztg. 1932, **56**, 383). (*b*) Raschig leads a rapid current of CO_2 through the nitrite solution, adds 10 c.c. 10% KI solution, waits 2–3 minutes and then acidifies with 1 c.c. of sulphuric acid (490 g./l.). After further 2 minutes standing the liberated iodine is titrated with $N/10$ thiosulphate (Ber. 1905, **38**, 3911). *Sulphite and nitrite* in presence of sugar: 10 c.c. $N/10$ iodine containing 1·0 g. $CaCO_3$ in suspension is titrated with the solution of the pickling salt, this gives SO_2 only. Nitrite in the titrated solution is then found by Raschig's method—Peltzer-Grossmann's cannot be used at this stage.

If sulphites are present Sherratt (Analyst, 1937, **62**, 267) reduces nitrate and nitrite by adding hydrazine sulphate to a strongly alkaline solution which is then boiled in a current of inert gas, phosphoric acid is added and the SO_2 boiled off and collected in H_2O_2 in the usual way.

Pflücker (Z. Unters. Lebensm. 1934, **68**, 196) recommends the removal of nitrite from a mixture with nitrate by Fischer and Steinbach's method (Z. anorg. Chem. 1912, **78**, 134) in which the concentrated solution is added to a small flask containing a mixture of methyl alcohol and of sulphuric acid (1:10), a current of CO_2 is then passed through the liquid until all the nitrite is removed as $MeNO_2$, b.p. $-12°$, the excess of methyl alcohol is evaporated on the water bath and the residual liquid tested for nitrate. Eegriwe (Z. anal. Chem. 1926, **69**,

384) tests for nitrites and nitrates by a sensitive reaction with Safranine AN extra, B or T.

Lactic Acid is not prohibited in Public Health (Preservatives, etc., in Food) Regulations possibly because of its formation by fermentation of sugar in presence of common salt in the manufacture of sauerkraut and other pickles. Serger and Clarck (Konserven-Ind. 1931, **18**, 375) state that lactic acid alone does not prevent the growth of moulds. As regards taste 1 part of acetic acid is equivalent to 1·28 parts of lactic acid. Katz (Bakers' Weekly, 1934, **82**, 37) added lactic acid to bread dough to arrest the development of spores of *B. mesentericus*, the organism which causes " ropiness." For lactic acid in the manufacture of cheese (*see* Vol. II, 526*c*). According to Rost (Arb. Reichsgesundh.-Amt. 1917, **50**, 405) lactic acid is not more irritant than tartaric and citric acids and is a satisfactory addition to food. It is a natural constituent of fruits, apple (max.) 9·1, blackberry (max.) 20·2 mg./100 g. (Hillig. J. Assoc. Off. Agric. Chem. 1937, **20**, 303 ; *cf.* 130); Yoghurt contains 2% (Mazhar *et al.* Chem.-Ztg. 1932, **56**, 46), bread about 0·3%, wine 0·05–0·5%, beer 0·3–0·8% (Bicker, Deut. med. Woch, 1932, **58**, 1562). For uses of lactic acid, *see* Serger and Clarck, Kälte-Ind. 1920, **17**, 351 ; 1921, **18**, 375. Fabian and Wadsworth (Food Res. 1939, **4**, 499, 511, 521) state that in pickles the total acidity should be not less than 2% as AcOH, of which 20–40% may be lactic acid calculated as AcOH. Lactic acid alone is far inferior to AcOH.

Detection.—There are several tests depending on colour reactions for acetaldehyde which is formed when lactic acid is oxidised. Herzog (Annalen, 1907, **351**, 263) oxidises silver lactate with iodine and collects the acetaldehyde formed in a little water in a test tube, to this is added a few drops of sodium nitroprusside solution and piperidine, a blue coloration turning violet, red and finally yellow, on addition of 1 drop of NaOH indicates acetaldehyde. Formaldehyde and furfuraldehyde do not give the reaction, malic acid, however, yields acetaldehyde when oxidised.

Denigès (Bull. Soc. Chim. 1909, [iv], **5**, 647) heats 0·2 c.c. of test solution (less than 2% concentration) with 2 c.c. sulphuric acid for 2 minutes in a water bath, and after cooling adds 2 drops of a 5% guaiacol solution in alcohol, lactic acid gives a magenta colour, 0·01 mg. a pink coloration. The guaiacol may be replaced by other phenols of which *p*-cresol, 1% solution, is the most sensitive (Capelli, Amer. Chem. Abstr. 1926, 3732). For a colour reaction with KCNS and HCl, not discharged by $HgCl_2$ *see* Germuth, Ind. Eng. Chem. 1927, **19**, 852. Fletcher and Gowland Hopkins describe a colour reaction with H_2SO_4, $CuSO_4$ and thiophen (J. Physiol. 1907, **35**, 247 ; J.C.S. 1907, **92**, ii, 373).

Microchemical.—Behrens-Kley, " Organische Mikrochemische Analyse " (2nd ed., L. Voss, Leipzig, 1922) recommends the formation of cobalt lactate and of cobalt lead lactate, rather than zinc lactate. Klein and Wenzl (Mikrochem. 1932, **11**, 73) use the Zn, Cu and Th salts. Griebel and Weiss (Z. Unters. Lebensm. 1928, **56**, 158) oxidise lactic acid to acetaldehyde with $KMnO_4$ in a micro beaker (Griebel, *ibid.* 1924, **47**, 438) and add *p*-nitrophenylhydrazine, and may be used (Brady and Elsmie, Analyst, 1926, **51**, 77). For " Estimation," *see* Smith, Analyst, 1938, **63**, 777.

Benzoic Acid is recorded as a preservative in beer worts (E. von Meyer and Kolbe, J.C.S. 1876, i, 959) about the time of its first large scale production from benzotrichloride (Lunge and Petri, Ber. 1877, **10**, 1275). Certainly since this date and possibly earlier it has been a popular preservative. Benzoic acid was studied by Miquel, and Hehner in 1891 comments on its extensive use for preserving foods. Restricted amounts of benzoic acid are permitted in certain beverages by the Preservatives in Foods Regulations (*v. infra*). It has therefore been in continuous use for at least 64 years and no other synthetic organic preservative may be used in Great Britain at the present time. (For an account of its antiseptic action, *see* DISINFECTANTS, Vol. IV, 28). The pharmacology of benzoic acid has been thoroughly investigated. Taken internally it is detoxicated by conjugation with glycine to form the harmless excretory product *hippuric acid* (for this defensive process, *see* B.P.C. 1934, 16; C. R. Harington, J.C.S. 1940, 119). The extensive use of benzoic acid and sodium benzoate for preserving food in the U.S.A. led to Wiley's researches (U.S. Dept. Agric. Bureau of Chem. Bull. No. 84, Pt. 4, 1908) in which these substances were described as injurious. Accordingly their use was prohibited by Food Inspection Decision, No. 76 of 13/7/07. However, the opposition of manufacturers was followed by the issue of F.I.D. No. 89 which restored their legality pending decision by a Referee Board. The Board reported that in the quantities added to foods, sodium benzoate was harmless. No attempt was made to reconcile the two opinions, and F.I.D. No. 104 and 107 both of 1909 permitted additions of sodium benzoate to foods (Folin, " Preservatives and other Chemicals in Foods," Harvard University Press, 1914). For a review of the literature, especially German references, *see* Tillmans " Handbuch der Lebensmittelchemie," 1933, I, 997. J. C. Krantz (J. Assoc. Off. Agric. Chem. 1936, **19**, 205; Amer. J. Pharm. 1936, **108**, 252) reports benzoic acid in 1:900 dilution as effective against moulds and bacteria; sodium benzoate even at 1% gave poor results in neutral media (Lucas, J. Amer. Med. Assoc. 1910, **54**, 759), even good brands may impart a slightly objectionable flavour at concentrations of 0·05–0·1% (Tressler, Joslyn and Marsh, " Fruit and Vegetable Juices," New York, 1939, p. 35).

Detection and Estimation.—(For qualitative tests, *see* Vol. II, 570*b*). A new method for determining benzoic acid and a review of the literature were published by Monier-Williams (Reports on Public Health and Medical Subjects, No. 39, H.M. Stationery Office, 1927; Analyst, 1927, **52**, 572). The author describes the steam distillation of the fruit etc., immersed in saturated NaCl solution acidified with H_3PO_4, the oxidation of impurities in the distillate with $KMnO_4$, and finally extraction with a solvent and subliming the extract as benzoic acid which is weighed. Mix (J. Assoc. Off. Agric. Chem. 1939, **22**, 305) modifies the method and can recover added 0·05 g. BzONa in control experiments to ±0·0075 g.

Monier-Williams states that Mohler's is the most sensitive qualitative test (Grossfeld, Z. Nahr. Genussm. 1915, **30**, 271). A colorimetric modification has been devised by Illing, Analyst, 1932, **57**, 244; 1939, **64**, 586), the stages are—nitration of benzoic acid to dinitro and reduction to diaminobenzoic acid, addition of ammonia and colorimetry of the orange-red solution. Another, but less delicate test is Jonescu's (J. Pharm. Chim. 1909, [vi], **29**, 523; Z. Nahr. Genussm. 1910, **19**, 137). This depends on the oxidation of benzoic acid to salicylic acid. The steam-distillate, from the sample immersed in dilute H_2SO_4, is extracted with ether, and the dry extract dissolved in 1 c.c. warm water; 1 drop of 0·3% H_2O_2 and 1 drop of $FeCl_3$ 2·9%, are added and the solution then heated in a waterbath. In the absence of phenolic bodies and of saccharin, the production of a violet colour indicates benzoic acid. Leather (Analyst, 1931, **56**, 299) has described a rapid test based on Hink's method (*ibid.* 1913, **38**, 555). In one food laboratory the following method has been found convenient: the benzoic acid is separated from the sample by steam distillation in presence of $CaCl_2$ and HCl (Nicholls, *ibid.* 1933, **58**, 4) and extracted from the distillate with ether, the crude benzoic acid after purification with $KMnO_4$ is eventually oxidised by H_2O_2 to salicylic acid which is determined colorimetrically with $FeCl_3$ (Nicholls, *ibid.* 1928, **53**, 19) as modified by Edwards, Nanji and Hassan (*ibid.* 1937, **62**, 172). Gangl and Lorenz (Österr. Chem.-Ztg. 1934, **37**, 90, 99) precipitate proteins with Carrez reagents ($K_4Fe(CN)_6$ and $ZnSO_4$) at alkaline reaction, filter, acidify the filtrate, shake with dilute NaOH and add a solution of KOH in *iso*propyl alcohol to precipitate BzOK; esters of *p*-hydroxybenzoic acid remain in solution but the free acid yields an insoluble K salt. The separation is effected by heating to 100° with 5% $KMnO_4$, BzOK is not altered but the hydroxy acid is decomposed. (For a simpler method of extraction, *see* Applied Chemistry Reports, 1925, **10**, 536.)

Benzoic Acid Group of Preservatives.—There are no less than eight now well-known preservatives and two sweetening agents which are soluble in ether and are separable from foodstuffs by the methods adopted for benzoic acid. (The sweetening agents must be considered here owing to their effect on the tests for preservatives.) The group includes the following acids: benzoic, salicylic, cinnamic, *p*-hydroxybenzoic, *p*-chlorobenzoic, *o*-chlorobenzoic; the esters: "*Nipagin M*," methyl *p*-hydroxybenzoate; "*Nipagin A*" the corresponding ethyl and "*Nipasol*" the corresponding propyl ester; the sweetening agents saccharin and dulcin (*q.v.v.*). The esters mentioned and their Na salts together with the benzyl ester, were patented and introduced by Sabalitschka (Z. angew. Chem. 1929, **42**, 936; Pharm.-Ztg. 1930, **75**, 454). Sodium *p*-chlorobenzoate known as "*Mikrobin*" was recommended for fruit juices (v.d. Heide *et al.*, Z. Unters. Lebensm. 1927, **53**, 487). For other esters, trade names and tests, *see* Jansen, Chem. Weekblad. 1936, **33**, 239.

The tests of T. von Fellenberg, *et al.* (Mitt. Lebensm. Hyg. 1932, **23**, 111) distinguished between *p*-hydroxybenzoic acid and benzoic acid, and the esters of the former acid were separated from benzoic acid and salicylic acid by R. Fischer and Stauder (Mikrochem. 1930, **8**, 330). Systematic separations of the 11 substances of the " benzoic acid group " have been described by R. Fischer (Z. Unters. Lebensm. 1934, **67**, 161). The method begins with the ether solution of the preservatives (obtained by known means from the food-stuff) which is shaken with dilute NaOH, only dulcin remains in the ether (I). The aqueous layer is acidified and extracted several times with light petroleum (II) which leaves only *p*-hydroxybenzoic acid and saccharin in the aqueous solution from which they are removed by extraction with ether (III). Each extract after drying with Na_2SO_4 is evaporated drop by drop in a small dish (diam. 14 mm. height 4–5 mm.; *cf.* R. Fisher *et al.*, *ibid.* 1931, **62**, 658). Microsublimations are then carried out in a simple modification of the micro-melting-point apparatus (Kofler and Hilbck, Mikrochem. 1931, **9**, 38; Fischer, 1933, **13**, 123) and observations made of the sublimation temperatures (S.T.), m.p., extinction with a polarising microscope and chemical reactions.

EXTRACT II.

	S.T. *ca.* °C.	M.p. °C.	Extinction.
1. Benzoic acid .	55	121	∥
2. "*Nipagin M*" .	70	α110; β126	∥[1]
3. Ethyl *p*-hydroxybenzoate .	70	116	∥
4. "*Nipasol*" . .	70	97	∥
5. *o*-Chlorobenzoic acid . . .	75	142	∥
6. Salicylic acid .	80	157	—
7. Cinnamic acid .	90	133	∥
8. *p*-Chlorobenzoic acid . . .	95	236	∥

[1] Polymorphic, Amer. Chem. Abstr. 1939, 6274.

EXTRACT III.

	S.T. *ca.* °C.	M.p. °C	Extinction.
9. *p*-Hydroxybenzoic acid .	135	213–214	—
10. Saccharin . .	150	221	∥

EXTRACT I.

	S.T. *ca.* °C.	M.p. °C.	Extinction.
11. Dulcin . . .	130	173	—

If vanillin is present it would interfere and is removed by shaking the original ether solution with semicarbazide hydrochloride and sodium acetate. The alcohol radicles of the esters are identified by saponification, oxidation of the alcohol obtained to the aldehyde followed by the application of aldehyde reagents, dimedon, *m*-nitrophenylhydrazine and thiosemicarbazide.

Valencien and Deshusses (Mitt. Lebensm. Hyg. 1939, **30**, 88) estimate the esters bromometrically. Monier-Williams (Report, 1927, **30**, 31) points out that to some extent saccharin may be changed during the analysis into ammonium sulphobenzoate, by the action of hot acids. The alternative extraction of the food-stuff with $NaHCO_3$ avoids this difficulty. Sabalitschka (Mikrochim. Acta, 1937, **2**, 111) describes an alkaline extraction of preservatives from fatty food-stuffs. The method of Diemair *et al.* (Mikrochem. 1938, **25**, 247) applies to meat and fish. Edwards, Nanji and Hassan (*l.c.*) rely on reactions for identifying *p*-hydroxybenzoic acid and its derivatives, as do Stevenson and Resuggan (Analyst, 1938, **63**, 152) and P. von Aufschnaiter (Amer. Chem. Abstr. 1939, 1439).

The esters are permitted preservatives in Norway, Hungary, Jugo-Slavia, Roumania and Germany (Sabalitschka, B. 1937, 977); according to the same author (Z. Unters. Lebensm. 1939, **77**, 256) they have anti-oxidant properties. The effective antiseptic concentrations of the esters in Turtiainen's experiments (Zentr. Bakt. I, 1937, **139**, 98) were: benzyl ester ("*Solbrol Z.*"), 0·002–0·008%; propyl ester, 0·05%; methyl ester, 0·25%.

Alcohol (*v.* ALCOHOL, ALCOHOLOMETRY).—If methyl alcohol is detected in ethyl alcohol used for preserving, the addition of methylated spirit may be the explanation (for the usual tests, some tedious, *v.* Vol. I, 184*a*, 191*c*). A rapid preliminary test is described by Eegriwe (Mikrochim. Acta, 1937, **2**, 329); to 1 drop of 40 vol. per cent. alcohol add successively 1 drop of 7% phosphoric acid, 1 drop of 5% $KMnO_4$ and after 1 minute particles of sodium bisulphite until the solution is colourless, 4 c.c. H_2SO_4 (15:10 vol. H_2O) are now admixed followed by a few particles of *chromotropic acid*, the solution is heated to 60° for 10 minutes, allowed to cool and observed after 5 minutes. A violet-pink colour indicates formaldehyde and hence methyl alcohol, limit 3·5μg. in a dilution 1:13,600. Ordinary alcohols and acetaldehyde do not interfere, glycerin gives a yellow colour with a green fluorescence, sugars give a yellow colour, the test would be carried out with a distillate. It should be mentioned that T. von Fellenberg found methyl alcohol in Swiss liqueurs distilled from fermented fruits (Biochem. Z. 1918, **85**, 45) and Flanzy's method (Compt. rend. 1934, **198**, 94) detects 0·1% MeOH in fermented liquors.

Sugar.—The preservative effect of sugar, as of salt and saltpetre, is due to the osmotic pressure of concentrated solutions. This property of sugar solutions is well shown in the case of jams, which, when boiled to a concentration of about 70–72% (depending on the percentage of insoluble matter present), are not susceptible to mould growth, provided the jams are in contact with an atmosphere of relative humidity not higher than 82%. Any deposit of moisture on the surface produces locally a less concentrated sugar solution which allows moulds to grow.

Salt, sodium chloride; the osmotic effect of a salt solution is much greater than that of a sucrose solution of equal concentration owing to its lower molecular weight, 58·4:342·3, and dissociation into ions. When immersed in a salt solution the cell wall of the bacillus behaves as a semipermeable membrane and the cell is deprived of water when the outer liquid has a higher osmotic pressure than the cell contents, thus the inhibitory effect is due to partial dehydration of the proteins in the bacterial cell (Medical Research Council, " System of Bacteriology," III, p. 83). By this process the growth of most bacilli and spores is inhibited, the halophiles have, however, exceptional resistance. (For examples in practice, *see* Macara, *l.c.* 662, 677; for history of salt, *see* C. G. Gümpel, " Common Salt," London, 1898, J. J. Manley, " Salt and other Condiments," London, 1884). Although salt is a preservative it may itself be contaminated with bacteria (Milne, Pharm. J. 1938, **140**, 81).

Glycerin is a permitted preservative in the Public Health (Preservatives, etc., in Food) Regulations. Pharmaceutical extracts of glands and vaccines, *e.g.* calf lymph, contain considerable amounts. Diluted it is a component of culture media for tubercle and other bacteria. It may be sterilized by heating for 1 hour to 150°. Its efficiency as a germicide has been questioned by Ruediger (J. Amer. Med. Assoc. 1915, **64**, 1529) and by Goodrich (Pharm. J. 1917, **98**, 453; Brit. Med. J. 1917, i, 647). Fine and Olsen (Ind. Eng. Chem. 1928, **20**, 652) state that baked cereal products containing 0·5% glycerin can be stored in a warm climate without developing a " tallowy " taint.

Detection.—Frehden and Chen-Hua Huang detect glycerine by concentrating the solution at 100° in a micro-crucible, crystallised oxalic acid is then added and the crucible heated to 105°. The contents are then mixed with saturated alcoholic hydroxylamine hydrochloride, rendered alkaline with alcoholic KOH and heated to start the reaction, acidified with alcoholic HCl and a drop of $FeCl_3$ added, a violet colour indicates the hydroxamic acid derived from monoformin if glycerin was present in the solution, limit 40μg. (Mikrochem. 1934, **15**, 12). Täufel and Thaler (Z. anal. Chem. 1933, **95**, 235) have improved the acraldehyde test: the dried aqueous extract, evaporated with excess of a paste of lime, is treated with excess of absolute alcohol and ether and the dry extract from this solvent is distilled with crystallised phosphoric acid. The distillate is oxidised with 3% hydrogen peroxide and conc. hydrochloric acid, and the excess of oxidising agent removed by successive treatment with potassium iodide followed by sodium thiosulphate. The epihydrinaldehyde formed from any acraldehyde present is then detected by the red colour obtained by addition of phloroglucinol in ether.

Determination.—Alfend (J. Assoc. Off. Agric. Chem. 1932, **15**, 331; Amer. Chem. Abstr.

1932, **26**, 5352) reports collaborative work on the determination of glycerin in egg products. The method previously found successful for meat products was unsatisfactory, especially in presence of added sucrose, the latter difficulty was not entirely overcome in a considerably simplified method based partly on the A.O.A.C. method for glycerol in vinegar. At one time milk was liable to contain glycerin added as a preservative, 2% was sufficient according to Wanklyn and Eassie's patent.

Boric Acid.—Boracic acid, H_3BO_3; borax, $Na_2B_4O_7,10H_2O$ (*v.* BORON, Vol. II, 47 and 49; DISINFECTANTS, Vol. IV, 20). Borax, now forbidden, was one of the earliest preservatives to be studied. J. Pringle, P.R.S. (Phil. Trans. 1749–50, **46**, 525) made comparative experiments on the effect of different salts in retarding the putrefaction of small pieces of beef immersed in the solution " and kept at about the degree of human heat." A 6·2% solution of common salt was the standard; borax was 12 times more efficient, 5 grains of borax having the same effect as 60 grains of salt. According to Sieber (J. pr. Chem. 1879, [ii], **19**, 433), a 2% solution of boric acid (300 c.c.) retarded the putrefaction of 50 g. minced ox pancreas for 3 days. Miquel's experiments (Moniteur Sci. 1872, [iii], **14**, 170) with 1 litre quantities of neutralised beef broth to which preservatives were added, showed the following additions in grams. to be equivalent: hydrogen peroxide, 0·50; salicylic acid, 1·00; benzoic acid, 1·10; boric acid, 7·50; phenol 3, mineral acids 2–3 g. Later determinations were more exact, but these and similar publications may explain the wide use of preservatives from the 1870's onwards.

Boric acid preservative was reported in milk and beer by Hirschberg (J.C.S. 1873, **26**, 100; 1876, i, 413). Its use spread to preserving cream, meat, sausages, fish, etc., and continued to be the subject of numerous papers, analytical or pharmacological until the present time; although the practice has been illegal in this country since 1927–28. The Report of the Departmental Committee on the Use of Preservatives and Colouring Matters in Food, 1901, Appendix VI, records analyses made by different observers. The maximum percentages of boric acid determined in different food-stuffs were: milk, 0·91; condensed milk, 0·50; cream, 0·80; butter, 1·6; margarine 1·0; sausages, 1·14; ham, 0·66. Of a total of 4,251 samples comprising 26 classes of foods, examined in the Government Laboratory, 1,247 were preserved with boric acid (p. xi). Much of the medical evidence before the Departmental Committee of 1901 did not condemn the use of boric acid preservative (Tunnicliffe *et al.*, *ibid.* 264, Appendix VI), although other authorities had already considered its presence in food to be objectionable (Lancet, 1879, i, 70; 1886, ii, 1142; 1887, ii, 333, 342, 392). Numerous investigations showed a cumulative effect of boric acid, 50% of a single dose being excreted in 12 hours but the remainder not entirely in 18 days (Neumann, Arb. Reichsgesundh.-Amt. 1903, **19**, 89). Other workers (*e.g.* Rost, *ibid.* **19**, 1) reported irritant effects of boric acid on the digestive tract, confirmed by Wiley (U.S. Dept. Agric. Bureau of Chemistry, Bull. No. 84, Pt. 1. Boric Acid and Borax, 1904).

Boric acid detection and estimation has been discussed in Vol. II, pp. 52, 53, and some further references for boric acid in food-stuffs may now be added. A new microchemical test is yohimbine borate (Martini, Mikrochem. 1939, **26**, 221). A. S. Dodd (Analyst, 1927, **52**, 463; 1929, **54**, 19, 282, 645, 715; 1930, **55**, 23), who has made a critical study of Thomson's titration method, indicates precautions necessary in ashing the sample, removing phosphates and in avoiding losses of H_3BO_3 when boiling to remove CO_2. Further work has been carried out by Burns Brown (*ibid.* 1936, **61**, 671) and by Alcock (*ibid.* 1937, **62**, 522). The application of the method to butter, cider, dried fruit, eggs, milk and meat paste is to be found in H. E. Cox, " Chemical Analysis of Foods," 2nd ed., Churchill, London, 1938. Experience particularly valuable for the legal aspect is recorded in J. F. Liverseege's " Adulteration and Analysis of Foods and Drugs," Churchill, London, 1938, and in the 7th edition (revised by H. E. Cox) of A. and M. Wynter Blyths' " Foods," C. Griffin, London, 1927. For early references on the antiseptic properties of boric acid and of borax, *see* Gmelin-Kraut, " Handbuch der anorganischen Chemie," article Boron.

Salicylic Acid (*v.* Vol. IV, 28*d*) was formerly often added as a preservative to beer, jam, wine, mincemeat, etc.; its use is forbidden in this country since 1927. In a concentration of 0·1–0·2% it suppresses yeast fermentation (Wehmer, Zentr. Bakt. II, 1902, **9**, 189) and preserves meat; mincemeat, however, only for 1 or 2 days (Kickton, Z. Nahr. Genussm. 1907, **13**, 534). When taken internally it becomes conjugated with glycocoll and is excreted as salicyluric acid in the urine (Piccard and Beck, Ber. 1876, **8**, 817). It is more irritating than benzoic acid in the digestive tract and the majority of medical authorities would disqualify salicylic acid as a preservative, although Christian (Hyg. Rundsch. 1908, 1321) observed no serious effects except with large doses (*cf.* Wiley U.S. Dept. Agric., Bureau of Chemistry, Bull. No. 84, Pt. 2, 1906).

The large scale manufacture of synthetic salicylic acid began in 1874; Kolbe soon after discovered its antiseptic properties (J.C.S. 1875, **28**, 460). Muter detected the addition of the acid to milk (Lancet, 1877, i, 105). The same Journal approved its addition to beer (*ibid.* 1886, ii, 1142). Miquel (*l.c.*) found its antiseptic effect slightly greater than that of benzoic acid. By 1891 O. Hehner considered that sulphurous acid and benzoic acid were replacing salicylic acid (Lancet, 1891, i, 96). In Holland its addition to food was already forbidden in 1888. In 1901, out of a total of 4,251 samples examined in the Government Laboratory, 320 were preserved with salicylic acid. (Departmental Committee on Preservatives Report, 1901, xi.) The maximum percentage in jam was 0·12 and in British wines 0·21 (*ibid.* Appendix VIII, Table L).

Detection and Determination.—Qualitative reactions are recorded in Vol. II, 570*b*. Several colorimetric methods are based on the reaction with ferric chloride. Nicholls (Analyst, 1928,

53, 19) gives a modified Jorissen's reaction—successive additions of 4–5 drops 10% KNO_2, 4–5 drops $CH_3 \cdot COOH$, 1 drop of 10% $CuSO_4$, on boiling, salicylic acid if present, gives a blood-red colour (Klett, Z. anal. Chem. 1903, **42**, 458). Sherman and Gross (Ind. Eng. Chem. 1911, **3**, 492) heat the mixture for ¾ hour on the water bath and claim to detect 1 p.p.m. in 5 c.c. by the violet colour due to salicylic acid. Monier-Williams' method can be used to remove salicylic acid (Public Health and Med. Subjects Report No. 39, 1927, 47). Jacobs (*op. cit.* 113) describes a general method for separating ether-soluble preservatives from food. T. von Fellenberg (detailed abstract J.C.S. 1910, **98**, ii, 906) has modified the method of Harry and Mummery (Analyst, 1905, **30**, 124) for estimating salicylic acid in jams, etc. The latter method is recommended by H. E. Cox (*op. cit.* 48). Jurány (Mikrochem. 1939, **26**, 314) can recognise as little as 0·4μg. salicylic acid from the microscopic appearance of the Ag salt, which can be distinguished from Ag benzoate. Several analysts have pointed out that *maltol* found in baked bread and malt coffee gives a violet colour with ferric chloride (Sherman, Analyst, 1910, **35**, 252; Backe, *ibid.* 253). Merl and Beitter's (Z. Unters. Lebensm. 1928, **56**, 472) discriminating test is Mandelin's reagent—5% ammonium vanadate in 95% sulphuric acid—which gives an indigo-blue colour with even 0·025 mg. of salicylic acid in the residue of a steam distillate, basified before evaporation.

Hydrogen Peroxide was frequently added to milk as a preservative before 1912 when its use in this food was forbidden; in cream (containing 35% or more of milk-fat), however, its presence was permissible until the Public Health (Preservatives, etc., in Food) Regulations of 1927 placed it under a general ban for all food-stuffs. There are certain organisms which are highly susceptible to H_2O_2 (Disinfectants, Vol. IV, 19). McLeod and Gordon (Biochem. J. 1922, **16**, 499; J. Path. Bact. 1923, **26**, 326, 332) have shown that these bacteria produce no *catalase*, an enzyme which decomposes H_2O_2 into H_2O and molecular oxygen. Admixture with tissues or with other organisms containing catalase is a protection against the germicidal effects of H_2O_2 (*v.* Catalase). It is remarkable that H_2O_2 can exist for long periods in milk; Hinks (Analyst, 1915, **40**, 482) added 0·2% to milk and found one-third of this amount still present after one year—or possibly an organic peroxide giving the same reaction. Hydrogen peroxide has been repeatedly stated to be a harmless antiseptic, the point has not been finally settled, but Chick (1901), Rosam (1902) and Bickel (Berliner Klin. Woch. 1911, 1467) objected to its use for preserving milk. Ried (Milchw. Forschung, 1931, **11**, 590) states that an objectionable taste frequently develops in food-stuffs to which H_2O_2 has been added. It was proved to be present in bottled chocolate beverages (Connecticut Agric. Experiment Station, Rept. Food Products, 1926) although claimed to be undetectable. Kühl (Pharm.-Ztg. 1937, **82**, 1214) found H_2O_2 was more effective in acid media. It has been used in glue as a bleaching agent with some preservative action (Pfanner, Chem. Zentr. 1936, II, 2276).

Detection and Estimation.—For a highly sensitive test, *see* Vol. II, 574*a*. Rothenfusser (Z. Nahr. Genussm. 1908, **16**, 590) tests for H_2O_2 in milk, first preparing a reagent by adding 6% lead acetate to fresh milk, filtering and mixing 9 vol. of filtrate with 1 vol. 30% acetic acid: 10 c.c. of the milk to be tested is mixed with 10 drops of the reagent and with 10–20 drops of 2% alcoholic benzidine solution. A blue coloration is seen if H_2O_2 is present, limit 0·16 p.p.m. The procedure is a reversal of the test for peroxidases, others of this type are described by Leach, "Food Inspection and Analysis," 4th ed., Chapman and Hall, London, 1920, 169. A quantitative iodometric method is described by Cox, *op. cit.* 250. The colorimetric method of Horst (Chem.-Ztg. 1921, **45**, 572) depends on the reaction between $FeSO_4$ and H_2O_2 in an inert atmosphere and colorimetric estimation of the $Fe_2(SO_4)_3$ with excess of NH_4CNS.

In Isaacs' colorimetric estimation (J. Amer. Chem. Soc. 1922, **44**, 1662) the solution of H_2O_2 is pipetted into a 50 c.c. flask already containing 30 c.c. of water and 10 c.c. 5% citric acid solution, after shaking 1 c.c. 10% ammonium molybdate is added, the mixture made up to the mark and compared with permanent colour standards prepared from potassium chromate solution. For a monograph on hydrogen peroxide, *see* W. Machu, "Das Wasserstoffperoxid," J. Springer, Vienna, 1937.

Sulphur Dioxide.—An incident in the Odyssey, xxii, is usually quoted to prove that the disinfectant action of burning sulphur was known in Homer's time. It has been employed for centuries as a disinfecting and bleaching agent. The preservative use of calcium bisulphite in breweries is described in J.C.S. 1872, **25**, 1130, and in the same year Calvert studied the effect of sulphurous acid on vibrios. A. H. Hassall reported the presence of one *per cent.* free sulphuric acid (derived from SO_2 fumigation) in samples of bleached musty hops ("Adulterations Detected," p. 505, Longmans, London, 1857). In a later work from the same publisher ("Food," 1876, 7) he states that sulphurous acid and sulphite of soda retarded decomposition of foods by combining with the oxygen of the air. Contact with air or, according to Gay-Lussac, with oxygen had been generally held to cause putrefaction. The extensive use of sulphurous acid or of sulphites for preserving wine, beer, meat, etc., led to researches on its alleged injurious physiological action (Walbaum, J.C.S. 1906 **90**, ii, 567; with Jacobi, *ibid.* 465). Wiley (U.S. Dept. Agric. Bureau Chem. Bull. No. 84, Pt. 3, 1907) objected to the use of sulphite preservatives. However, the fact that when swallowed small amounts of sulphites are rapidly oxidised to harmless sulphates, was an argument against his views. Prolonged experiments in the Reichsgesundheits-Amt. indicated that in the proportions used as preservatives, sulphurous acid had no harmful physiological effect. (For literature, *see* Tillmans, "Handbuch der Lebensmittelchemie," 1933, I, 1006.) The resistance to sulphurous acid and to sulphites of certain bacteria, yeasts and moulds is as 1:4:5 (Hailer, Arb. K. Gesundheits-Amt. 1911, **36**, 297; *cf.* Perry and Beal, Ind. Eng. Chem. 1920, **12**, 255). It has been alleged against the use of sulphurous acid that it improves colour and disguises fermentation or putrefaction of stale fruit or meat so that deception as to their quality has been practised.

The quantity of ripe fruit delivered to jam factories during the season so greatly exceeds the capacity of the plant that fermentation must occur unless the fruit is chilled or dosed with a preservative, here preferably sulphurous acid or a sulphite. When the fruit is boiled the sulphurous acid is oxidised or volatilised, and the colour of the fruit, which has been bleached by the preservative, is usually restored (Serger and Clarck, Chem.-Ztg. 1931, **55**, 838). Barker and Grove (J. Pomology, 1925, **5**, 50) state that fresh whole fruit will keep indefinitely in dilute sulphurous acid, 0·08–0·1% SO_2, and micro-organisms are still inhibited when the concentration sinks to 0·04% by absorption in the fruit. Cruess and Fong (Fruit Products J. 1926, **6**, No. 3, 13) have shown that sulphurous acid prevents the browning of apricots, pears, etc., due to exposure to air; about 1600 mg. SO_2 per litre permanently inactivates the peroxidase, although the organic peroxide which is responsible for the browning is temporarily inactivated by 60 mg. SO_2 per litre. A content of 3000 mg. SO_2 per litre gave good results in several months' storage in sealed containers (*ibid.* 1927, **6**, No. 11, 18) an amount not permitted in this country except for cherries for conversion into jam (*v. infra* Regulations). Cruess *et al.* (Hilgardia, 1931, **6**, 295) estimated that in acid juices 0·1% SO_2 will prevent growth, and 0·2% will prevent oxidation of the juice in a closed container. For sulphurous acid in beer, *see* BREWING, Vol. II, 102*d*; in cider, Vol. III, 127*c*.

Detection.—(Vol. II, 574*c*); with iodine (Bougalt and Cattelain, Z. anal. Chem. 1933, **91**, 381); with Fast Blue R (Eegriwe, *ibid.* 1926, **69**, 384); with indigo-carmine (Korenman, Mikrochem. 1936, **20**, 225).

Estimation (Vol. II, 666*d*). Monier-Williams (Report No. 43, Public Health and Med. Subjects H.M. Stationery Office, 1927) in this monograph describes the method which has been generally regarded as overcoming the difficulties of the estimation. The sample is placed in a flask containing dilute hydrochloric acid 20:500 and attached to a sloping inverted condenser, the upper outlet of which is connected to a series of three absorption vessels containing hydrogen peroxide neutralised to Bromophenol Blue. Before the introduction of the sample the dilute acid is boiled for a few minutes while a current of CO_2 is passed through the apparatus to remove air. After cooling and introduction of the sample, the liquid is boiled for 1 hour in a current of CO_2. The condenser water is then turned off to allow the condenser to become hot. The contents of the absorption vessels (1 Erlenmeyer flask and 2 Peligot tubes) are titrated with 0·1*N* $NaOH$ to Bromophenol neutrality. The sulphate thus obtained may be precipitated in the cold with $BaCl_2$. The method combines the advantages of several earlier methods. Iodometric titration of the SO_2 which often gave high results has been rejected. (The present writer found that rubber stoppers would give a small positive blank value to 0·1*N* iodine). Bromine water and iodine are not generally used for oxidising the SO_2, since these reagents oxidise also volatile sulphur compounds obtained on distilling onions, mustard, horseradish, and even fish (Masters and McCance, Biochem. J. 1939, **33**, 1304).

A. C. Chapman (Analyst, 1922, **47**, 204) suggested absorption in hydrogen peroxide which as Monier-Williams then found does not oxidise hydrogen sulphide in the cold. The sulphuric acid formed in the distillate is determined with standard *N*/10 alkali, but in many cases is preferably weighed as barium sulphate (Knapp and Phillips, *ibid.* 1928, **53**, 149; Järvinen, Z. Nahr. Genussm. 1925, **49**, 283). Several modifications were compared by Nichols and Reed (Ind. Eng. Chem. [Anal.] 1932, **4**, 79) who recommend (*a*) rapid heating with an electric heater, (*b*) HCl rather than H_3PO_4 to liberate SO_2, (*c*) gravimetric determination preferably in Monier-Williams' distillation method. Rapid distillation was recommended by a committee of chemists whose work is reported in the Analyst, 1928, **53**, 118, 130, 133, 136, 138, 142, 149, 157. The Committee's recommendations (*l.c.* 118–129) include a special still-head, reducing the time of distillation to 10 minutes for gelatin and to 20–30 minutes for hard fruits, and observations on titration with *N*/10 iodine. Black and Warren (*ibid.* 130) give the precautions necessary when interfering substances (nutmeg, mustard, ginger, etc.) are present. A convenient method of supplying de-aerated water is described by Freeland (*ibid.* 1930, **55**, 383). A rapid limit test (15–20 minutes) not affected by a number of substances which interfere in the original method has been described by Herd (*ibid.* 1930, **55**, 35). In a criticism of Miller's method, May (*ibid.* 1927, **52**, 526) advises longer boiling to liberate all the SO_2 from dried fruit. Schätzlein (Z. Unters. Lebensm. 1940, **79**, 164) rejects the pumice powder employed by Rothenfusser (*ibid.* 1929, **58**, 98) to facilitate distillation, before determining SO_2 as benzidine sulphate in the oxidised distillate.

Formic Acid has been used as a cheap substitute for benzoic acid although inferior in preservative effect (Neisser and Tillmans, Konserven-Ind. 1926, **13**, 362). It occurs naturally about 2·8 mg. in 100 g. in orange juice and in honey, 10 times this amount has been added to preserved honey. Formic acid is formed in the caramelisation of sugar, as much as 1200 p.p.m. has been found, and the importation of the consignment prohibited.

Detection (Vol. II, 569*d*).—Formic acid is reduced by Mg powder and HCl to formaldehyde which is detected with chromotropic acid (*v. supra*, $MeOH$ in $EtOH$) or with other reagents.

Determination.—Grossfeld and Payfer (Z. Unters. Lebensm. 1939, **78**, 1) extract the diluted acidified food-stuff with ether in an extractor and distil the ether residue with light petroleum. $H{\cdot}COOH$ in the distillate is oxidised with $HgCl_2$ and the Hg_2Cl_2 weighed (*cf.* Reid and

Weihe, Ind. Eng. Chem. [Anal.], 1938, **10**, 271, who estimate the CO_2 evolved on oxidation with $Hg(OAc)_2$. T. von Fellenberg estimates $H{\cdot}COOH$ in the ether residue (Mitt. Lebensm. Hyg. 1936, **27**, 182), Kobzarenko (Amer. Chem. Abstr. 1940, 1752) publishes a bromometric method.

Anti-oxidants, *e.g.* quinol (J.S.C.I. 1928, **47**, 819), have been found to delay the rancidity of fats (*s.a.* Wagner *et al.* Ind. Eng. Chem. 1931, **23**, 40) and the addition of quinol was successful with salted herrings. Preiss (Z. Unters. Lebensm. 1934, **67**, 144) found that steam distillation of a sample previously acidified and mixed with ferric chloride solution enabled quinol to be estimated by iodometric titration of the quinone in the distillate. In a review of the subject C. H. Lea (D.S.I.R. Food Invest. Spec. Rept. No. 46, 1938, 174) discusses naturally present anti-oxidants and also hydroquinone and other reagents which are not permissible as additions to food-stuffs (*see also* Monier-Williams, " Food and the Consumer," *op. cit.*).

Diacetyl and acetylmethylcarbinol occur in butter and their presence partly accounts for its flavour. When, however, these substances are additions, their estimation is important (*v.* Barnicoat, Analyst, 1935, **60**, 653; Schmalfuss and Werner, Z. Unters. Lebensm. 1938, **76**, 113; Wilson, J. Assoc. Off. Agric. Chem. 1938, **21**, 427). Hammer found 0·0002–0·0004% of diacetyl in high-class butter and about 10 times these amounts of the parent substance acetylmethylcarbinol (Winton and Winton, " Structure and Composition of Foods," 1937, III, p. 165). At a concentration of 0·1 g. per L. diacetyl inhibits the growth of micro-organisms (Lemoigne and Monguillon, Ann. Falsif. 1935, **28**, 278). The amount of diacetyl may vary from a trace to 0·4 mg. per kilo in butter samples from the same source (Amer. Chem. Abstr. 1939, 2234).

Natural Occurrence of Preservatives in Large Traces.

The Ministry of Health (Circular 806 of 29/6/1927) notified local authorities that traces of some of the prohibited preservatives and colouring matters are normal constituents in traces in some foods, *e.g.* boric and benzoic acids, also copper in peas, such traces are less than the quantities for effective preservation or colouring (Ministry of Health, Ann. Rept. Chief Med. Officer, 1926, p. 200).

A. C. Chapman (Analyst, 1927, **52**, 215) obtained substances giving the reactions of formaldehyde and of benzoic acid from heated sugar. Dill and Clark's (J. Assoc. Off. Agric. Chem. 1926, **9**, 117) tests indicated 0·01% formaldehyde in some canned crustacea. Tests on salt ling indicated formaldehyde, 480 p.p.m., by Schryver's method although none had been added in curing the fish (Reay, Analyst, 1936, **61**, 78).

Mattick (Analyst, 1930, **55**, 37) examined numerous samples of sterilised milk which gave positive tests for *p*-cresol, believed to be due to a bacillus. Hansma and Kniphorst (Chem. Weekblad, 1932, **29**, 140, 205) tested extracts of rye bread which gave a positive reaction for salicylic acid. The coloration is attributed to 3-hydroxy-γ-pyrone derivatives, formed during baking.

Foreign Substances in Foods are discussed by Hughes (Chem. and Ind. 1935, **54**, 746); those which have been detected at different times include benzoyl peroxide (*v.* Vol. II, 81*c*), persulphates, iodates, bromates and sodium phosphate; the first four substances are not among the permitted preservatives. For their bleaching action and for the motive for adding sodium phosphate the original paper should be consulted. Drummond (Chem. and Ind. 1935, **54**, 744) discriminates permissible from unjustifiable additions to food.

For a long period chemical preservatives were added to food-stuffs with little risk of detection or prosecution. With his daily meals an Englishman frequently swallowed more than one preservative. The commonest were boric acid and borax in milk, sausages and meat; salicylic acid or sulphites in beer, meat and jam; formaldehyde in milk and cream; benzoic and salicylic acids in sauces and beverages. Disregarding the traditional salt, sugar, etc., the general use of chemical preservatives which began about 1875 followed closely the first large scale manufacture of formaldehyde, benzoic and salicylic acids. Boric acid was available from Tuscany since 1807, and its preservative effects were known even earlier (p. 303*g*).

Popular imagination had been impressed by Pasteur's discovery (1863) that bacteria were the cause of putrefaction and by Lister's successful use of antiseptics in surgery (1867). In addition to a general if imperfect knowledge of " germs " there was a widespread belief that food which had an unpleasant smell could originate an epidemic. At the same time cheap chemicals were available which, in small amounts, could be mixed with food without the knowledge of the consumer, with the result that signs of decomposition of the food were not apparent for several days. These were the reasons that convinced the manufacturers or distributors of foods that the addition of preservatives was in the public interest as it certainly was to their own profit (*cf.* Drummond and Wilbraham, " The Englishman's Food," London, 1939, p. 386; Savage, " Food and the Public Health," London, 1919, p. 122). The gross carelessness in the collection, preparation, transport, distribution and handling of food-stuffs under dirty conditions which persisted up to quite recent times (Local Government Board Report of Inspectors of Foods, 1918–19, pp. 8, 9, " very large number of smaller factories . . . conditions unsatisfactory in the extreme ") was the cause of heavy bacterial infection of the food. The use of preservatives postponed investigation of the antecedent conditions and probably saved quantities of food from being thrown away. The effect of preservatives on bodily health was studied later. In the '60s of the past century, sulphurous acid or a sulphite was the chief chemical preservatives as shown by the work of the Food Committee of the Society of Arts, *e.g.* in Dewar's process (J. Soc. Arts, 1867–68, 16, 489), meat after immersion in B.P. sulphurous acid for 6 hours was dried below 140°F. Medlock (*ibid.* p. 52) injected carcases with calcium bisulphite. Reference works such as Watts, "Dictionary of Chemistry," London, 1863, I and II, 1864, and A. H. Hassall, "Adulterations Detected," Longmans, London, 1857, contain little or no information concerning the chemical preservatives generally used in the following decades. The great work of A. H. Hassall and "The Lancet" in combating adulteration of food prepared the way for the attack on preservatives. Credit for the opposition to preservatives must be given to later analysts, Muter, Hehner, Cribb, Liverseege and others. The rate of progress while knowledge of preservatives was slowly increasing is shown by the following summary of the action taken by various authorities and by the Government: Analytical Sanitary Commission of The Lancet, 1851–54, A. H. Hassall, "Food and its Adulteration," Reports of the Commission, 1855; Parliamentary Committee on Adulteration of Food, 1855. Sale of Food and Drugs Act, 1875. Section 3 of this Act provides that "no person shall mix . . . any article of food with any ingredient . . . so as to render the article injurious to health, with intent that the same may be sold in that state." Section 6 states "that no person shall sell to the prejudice of the purchaser any article of food or any drug which is not of the nature, substance and quality of the article demanded." There is no mention of preservatives in the Act and in the following Amending Acts; the public health is protected by penalising adulteration, but unless food mixed with preservatives can be proved to contravene Sections 3 or 6 the sale of such food is not forbidden. Public analysts appointed under the Acts of 1860 and 1869 continued the thankless task of detecting and estimating preservatives (in connection with their work in suppressing adulteration) with very inadequate support from the magistrates administering the Act until limited progress was shown by the Milk and Cream Regulation 1912 which prohibited the addition of any preservative to milk. Meanwhile two committees had undertaken protracted inquiries, a conference had been held and the Local Government Board published reports by its own officials on preservatives. The Reports of the Select Committee on Food Products Adulteration, 1894, 1895 and 1896, indicate the difficulty of Government action, owing to the diversity of opinion among medical men as to the effect of preservatives on the public health (1896, Lloyd, Q.279) Hehner said preservatives were unnecessary (*ibid.* Q.881). In the opinion of the Committee (*ibid.* vi) the evidence showed that antiseptics are added to almost all perishable food-stuffs and it would be difficult to prove that preservatives were injurious to health. The unequal incidence of the law was the subject of complaint at the Institute of Chemistry Conference on Adulteration (Intern. Health Exhib. 1884). Odling stated that although beer contained calcium bisulphite and no action was taken, dealers were prosecuted for selling milk containing boracic acid. Dupré said the souring of milk was a warning that the dairy was not clean and addition of preservative removed a safeguard.

A growing body of opinion that the food laws or their administration was gravely lacking as regards preservatives led in 1899 to the appointment of the first committee to hear evidence on preservatives as distinct from adulterants. The Report of the Departmental Committee (1901) appointed to inquire into the use of preservatives and colouring matters in food shows that the preservatives in general use were sulphites, boric acid, formalin and salicylic acid. There was much contradictory medical evidence as to the harmful effects of the three last mentioned (pp. xxiiii, xxiv). Witnesses testified to the value of chemical preservatives in protecting consumers from the evils of tainted or decomposing food, but the weight of scientific evidence was against the additions of chemicals to foods. The Committee held, however (p. xx), that some preserving means, not necessarily chemical, appears to be needed for a considerable portion of the perishable food supply, especially of the poorer classes. The issue, however, of refrigeration *versus* preservatives is not raised in this Report. It appeared that, although some public authorities prosecuted vendors of milk containing boric preservative, the policy of the authorities and the proportions of preservative considered permissible varied from place to place (p. xvi). The medical evidence on the effect of preservatives on health was contradictory, some witnesses could observe no disturbance of functions after protracted tests of formaldehyde (Q.3229, 3295), boric acid (p. xxiii) and salicylic acid (p. xxiv). Nevertheless the Committee put forward the following recommendations (p. xxx) —formaldehyde should be absolutely prohibited; salicylic acid permitted, provided the amount does not exceed 1 grain per lb. of food (per pint in a liquid); in cream, butter and margarine only boric acid and borax preservatives to be allowed, and in cream not exceeding 0·25% as H_3BO_3, in butter and margarine not more than 0·5%; the use of copper salts in "greening" of vegetables to be prohibited (one dissentient); the presence of preservatives to be declared on the label.

In the following decade 1901–11, these recommendations remained without legal force in Great Britain. Considerable research work, however, was carried out in the United States and in Germany. H. W. Wiley in the course of a long struggle against the use of preservatives published Bulletin 84 of the Bureau of Chemistry, U.S. Department of Agriculture, Parts 1–5, 1904–08, in which he attacked the common preservatives (*v.* Bibliography and individual preservatives). A bitter controversy followed in which Wiley's experiments were attacked by, among others, Liebrich ("Third Treatise on the Effects of Borax," Churchill, London, 1906). Doubt was cast on the findings of the 1901 Committee by the subsequent proof that the proportion of salicylic acid recommended was inadequate to prevent fermentation, while the maximum amount of boric acid permitted was twice the quantity usually found in food.

The Government action against preservatives recommenced in 1912 with Public Health (Milk and Cream) Regulations which prohibits the addition of any preservative substance to milk but permits only boric acid and hydrogen peroxide in cream containing more than 35% milk fat. An Amendment Order in 1917 limited H_3BO_3 to not more than 0·4%, no numerical limit is given for H_2O_2 but only traces were expected to remain in the cream. Apart from legislation, the officials of the Foods Section in the Medical Department of the Local Government Board (afterwards the Ministry of Health) issued a series of valuable reports which had an effect in checking the use of preservatives.

For many years public analysts (*v.* Bibliography) continued to protest against the additions of chemicals to food and the uncertainty of the legal position. W. G. Savage. ("Food and the Public Health," Cassell & Co., London, 1919, p. 38) said it was quite useless to prohibit certain specified preservatives as fresh ones would be supplied. The analyst must decide whether the presence of the preservative amounts to adulteration ("The Times" Food Number, 8 June, 1914). The appointment of the Departmental Committee on the Use of Preservatives and Colouring Matters in Food was a belated acknowledgment of public opinion. Their final Report, 1924, reviews the law of adulteration and remarks that "the proof that a preservative or colouring matter mixed with an article renders it injurious to health is not an easy, inexpensive or expeditious matter, and when established in one instance or in one court is not necessarily effective in other instances or in other courts . . . neither traders nor local authorities nor the public can definitely know what is permissible and what is not."

The Committee heard medical evidence on the effect of preservatives on health which, although unpublished, appears to have been contradictory in some respects. However, the wide range of biochemical knowledge available enabled the Report of 1924 to suggest regulations which have been, for the most part, adopted. The Public Health (Preservatives, etc., in Food) Regulations 1927 to 1939 relate to limited additions and only to certain foods of benzoic acid, sulphurous acid and nitrites (*see below*). Part II prohibits certain dyestuffs. The Regulations should be consulted for directions as to declaration of preservatives. The Committee's proposal did not receive legal sanction without opposition. It was said that, in the absence of preservatives, there would be great waste of food for which cold storage was not available. On the other side it was urged that dirty methods of collecting and preparing food were concealed by the use of preservatives.

THE FIRST SCHEDULE

PART I.—ARTICLES OF FOOD WHICH MAY CONTAIN PRESERVATIVE AND NATURE AND PROPORTION OF PRESERVATIVE IN EACH CASE.

The articles of food specified in the first column of the following table may contain the preservative specified in the second column in proportions not exceeding the number of parts (estimated by weight) per million specified in the third column:—

Food.	Preservative.	Parts per Million.
1. Sausages and sausage meat containing raw meat, cereals and condiments.	Sulphur dioxide.	450
*2. Fruit and fruit pulp (not dried) for conversion into jam or crystallised glacé or cured fruit as defined in items 6 and 7:		
(*a*) Cherries	Do.	3,000
(*b*) Strawberries and raspberries.	Do.	2,000
(*c*) Other fruit . . .	Do.	1,500
3. Dried fruit:		
(*a*) Apricots, peaches, nectarines, apples and pears.	Do.	2,000
(*b*) Raisins and sultanas	Do.	750
4. Unfermented grape juice and non-alcoholic wine made from such grape juice if labelled in accordance with the rules contained in the Second Schedule to these Regulations.	Benzoic acid	2,000
5. Other non-alcoholic wines, cordials and fruit juices, sweetened or unsweetened.	Either Sulphur dioxide or Benzoic acid.	350 600
*6. Jam (including marmalade and fruit jelly prepared in the way in which jam is prepared).	Sulphur dioxide.	40
7. Crystallised glacé or cured fruit (including candied peel).	Do.	100
*7a. Fruit and fruit pulp not otherwise specified in this Schedule.	Do.	350
†8. Sugar (including solid glucose) and cane syrups.	Do.	70
†8a. Cornflour (maize starch) and other prepared starches.	Do.	100
9. Corn syrup (liquid glucose)	Do.	450
10. Gelatine	Do.	1,000
11. Beer	Do.	70
12. Cider	Do.	200
13. Alcoholic wines. . . .	Do.	450
14. Sweetened mineral waters.	Either Sulphur dioxide or Benzoic acid.	70 120
15. Brewed ginger beer . .	Benzoic acid	120
16. Coffee extract	Do.	450
17. Pickles and sauces made from fruit or vegetables.	Do.	250

* Amended forms of items 2, 6 and 7 substituted, and new item 7a added, by Regulations of 1926.

† Amended form of item 8 substituted, and new item 8a added, by Regulations of 1927.

PART II.—COLOURING MATTERS WHICH MAY NOT BE ADDED TO ARTICLES OF FOOD.

1. *Metallic Colouring Matters.*

Compounds of any of the following metals:

Antimony,	Copper,
Arsenic,	Mercury,
Cadmium,	Lead,
Chromium,	Zinc.

2. *Vegetable Colouring Matter.*

Gamboge,

3. *Coal Tar Colours.*

Number in Colour Index of Society of Dyers and Colourists, 1924.	Name.	Synonyms.
7	Picric Acid.	Carbazotic Acid.
8	Victoria Yellow.	Saffron Substitute; Dinitrocresol.
9	Manchester Yellow.	Naphthol Yellow; Martius Yellow.
12	Aurantia.	Imperial Yellow.
724	Aurine.	Rosolic Acid; Yellow Coralline.

Provisional Regulations dated October 20, 1939,

Nitrites.

2. The Public Health (Preservatives, etc., in Food) Regulations, 1925, as amended shall be further amended as follows:

(1) The following additional proviso shall be inserted at the end of Article 4 (1) and at the end of Article 11 (1):

> "(iv) The provisions of this Article shall not apply so as to prohibit the presence of added sodium or potassium nitrite in bacon, ham and cooked pickled meat."

(2) The following paragraph shall be inserted after Article 4 (3):

> "(4) No person shall manufacture for sale or sell any cooked pickled meat, other than bacon and ham, which contains sodium or potassium nitrite in proportions exceeding two hundred parts per million calculated as sodium nitrite."

In prolonged correspondence in "The Times" in 1925, Sir William Pope led the opposition (22 January, 1925), he and F. W. Tunnicliffe (*ibid.* 23 January, 1925) and others considered boric acid a valuable and relatively harmless preservative. F. Gowland Hopkins, on the contrary, regarded boric acid as a cumulative poison. Paternó (Union intern. Chimie pure et appl., 4th Congress, Cambridge, 1923, p. 154) reported on the good health enjoyed by the workers in Ladarello where the air contained 8 mg. H_3BO_3/cu. metre outside the factory, the water supply 10 mg./l., potatoes 700 and bread 20 mg./kilo. However, the Committee accepted the experiments of Forster, Rubner and Rost as proving the harmful effects of boric acid.

Detection of Colouring Matters.—Nicholls (Analyst, 1927, **52**, 585) describes methods for detecting the colouring matters prohibited by the Regulations, 1925 to 1927, Part II. For all classes of dyestuffs, *see* Dyeing (Vol. IV, 147) and following tables which apply after extraction of the dye from the food and transference to an appropriate fibre. Mathewson, "Separation and Identification of Food Colouring Substances," U.S. Dept. Agric. Bull. No. 448, 1917, may also be consulted. The strongly antiseptic action, even in low concentrations, of some dyestuffs is described in Medical Research Council, "System of Bacteriology," I, 203 (1929).

Foreign Regulation of Preservatives.—In the United States, sodium benzoate or sulphurous acid are permitted in limited amounts (*cf.* the Federal Food Drug and Cosmetic Act which became effective in June, 1939); all imported foods as well as interstate commerce in foods are governed by this Act. Individual State laws, of which there are several, control only the production and sale of foods within the particular State (Fiene and Blumenthal, "Food Manufacture," Chemical Publishing Co., New York, 1938; for preservatives permitted in Germany, *see* Will, Deut. Apoth.-Ztg. 1939, **54**, 545; Gangl and Lorenz, Oesterr. Chem.-Ztg. 1934, **37**, 91). Hilton (*v.* Bibliography) published in 1934 a summary of the regulations of all the more important countries. The Report of the Departmental Committee, 1924, reviews the foreign regulations in force at that date.

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J. N. G.

FOOL'S PARSLEY (*v.* Vol. I, 160*d*).

"FORGENIN." A name applied to tetramethyl-ammonium formate.

FORMALDEHYDE, CH_2O. This substance, the simplest and least characteristic of the aliphatic aldehydes, is of the greatest technical importance in modern chemical industry. Although discovered in 1867 by Hofmann, it was not until 1892 that Kekulé isolated the monomer in a state of comparative purity.

Manufacture from Methanol.

Practically all the formaldehyde produced to-day is obtained by the catalytic vapour-phase oxidation by air of methanol, either synthetic or the wood distillation product. The equation:

$$CH_3{\cdot}OH+\tfrac{1}{2}O_2=CH_2O+H_2O$$

only expresses very approximately the overall effect taking place during the oxidation process. In actual practice, the reaction is complex and, in addition to oxidation, some formaldehyde is undoubtedly formed by dehydrogenation, while a portion is lost by decomposition into hydrogen and oxides of carbon.

The endothermic *dehydrogenation* of methanol is known to take place in the vapour phase at temperatures of 200°C. and above, under the influence of certain catalysts in accordance with the reversible equation:

$$CH_3{\cdot}OH \rightleftharpoons CH_2O+H_2-24{\cdot}7 \text{ kg. cal.},$$

the equilibrium constants of which have been determined by Ghosh and Chakravarty (J. Indian Chem. Soc. 1925, **2**, 142). Dehydrogenation can be effected with high efficiencies and high conversions per pass at temperatures of about 200°C. in the presence of freshly reduced copper (Sabatier and Mailhe, Ann. chim. phys. 1910, [viii], **20**, 344) or of a catalyst prepared from copper acetate and 1% of cerous nitrate (Ghosh and Baksi, J. Indian Chem. Soc. 1926, **3**, 415), but the life of the catalyst is usually short. Methyl formate is often an important product of the dehydrogenation of methanol over mixed copper catalysts (Frolich, J.S.C.I. 1928, **47**, 173T; Ivannikov and Sherko, J. Appl. Chem. Russia, 1933, **6**, 1148). In actual practice, the dehydrogenation process has not proved possible on a technical scale, largely because of rapid inactivation of the catalysts employed and also because of the simultaneous production of much by-product. However, processes involving dehydrogenation in the presence of metallic catalysts on porous supports (Backhaus, U.S.P. 1437483, 1922) and also in the presence of reduced metallic catalysts with steam as diluent (Carbide and Carbon Chemicals Corp., Canadian P. 363490, 1937) have been proposed. According to Natta and Strada (Giorn. Chem. Ind. Appl. 1932, **14**, 545, 551) formaldehyde may be produced with efficiencies of 80–90% by dehydrogenation of methanol in the presence of a large excess of carbon dioxide or carbon monoxide. These high efficiencies may be due, at least in part, to the reduction of partial pressure of the formaldehyde by the excess diluent with resulting diminished tendency to undergo further decomposition.

The mechanism of the controlled oxidation of methanol to formaldehyde was first systematically investigated by Orloff (J. Russ. Phys. Chem. Soc. 1907, **39**, 855, 1024; 1908, **40**, 796, 1590; Ber. 1909, **42**, 895) who concluded that the main reaction,

$$CH_3{\cdot}OH+\tfrac{1}{2}O_2=CH_2O+H_2O,$$

was followed by the secondary reactions,

$$CH_2O=CO+H_2,$$
$$CO+\tfrac{1}{2}O_2=CO_2$$
and
$$H_2+\tfrac{1}{2}O_2=H_2O.$$

However, Le Blanc and Plaschke (Z. Elektrochem. 1911, **17**, 45) noted (i) that the hydrogen produced always far exceeded in volume the sum of the oxides of carbon, (ii) that considerably less oxygen than is required by the theoretical equation may be used without serious diminution in the yield of formaldehyde, and (iii) that in the absence of added air, or oxygen, the activity of the catalyst diminished rapidly but could again be renewed by passage of air. For these, and other reasons, Le Blanc and Plaschke believed that the fundamental reaction is one of dehydrogenation, the hydrogen liberated being largely burnt to water. The addition of oxygen to the reaction mixture was thus regarded as necessary to supply heat and to maintain the catalyst in an active condition by a process of alternate oxidation and reduction. Similar conclusions were reached by Thomas (J. Amer. Chem. Soc. 1920, **42**, 867) who formulated the following individual reactions:

(1) $CH_3OH=CH_2O+H_2$ (dehydrogenation).

(2) $CH_2O=CO+H_2$ (decomposition of formaldehyde).

$$\left.\begin{array}{ll}(3) & H_2+\frac{1}{2}O_2=H_2O\\ (4) & CO+\frac{1}{2}O_2=CO_2\end{array}\right\}\text{(oxidation of hydrogen and carbon monoxide, occurring only partially).}$$

In addition to its effect in transforming an endothermic dehydrogenation into an exothermic reaction and in maintaining the activity of the catalyst, the air used may exert other influences favouring high yields of formaldehyde. By rapidly removing hydrogen from the sphere of reaction, the dehydrogenation process is allowed to proceed virtually to completion. In addition, the dilution of the reacting gases with large amounts of inert gas, namely nitrogen, reduces the partial pressure of the formaldehyde and thus probably minimises its tendency to undergo decomposition.

Formaldehyde was first produced by Hofmann (Annalen, 1868, **145**, 357; Ber. 1869, **2**, 152) by the incomplete combustion of methanol over a red-hot spiral of platinum wire. Subsequently, Volhard (Annalen, 1875, **176**, 128) and Tollens (Ber. 1882, **15**, 1629; 1883, **16**, 917) improved this method and endeavoured to control the temperature of the catalyst by regulating the flow of the mixture of air and methanol vapour. Platinised asbestos was found equally effective by Kablukoff (J. Russ. Phys. Chem. Soc. 1882, **14**, 194) while, later, platinum and palladium blacks were used by Orloff. Almost simultaneously, Loew (J. pr. Chem. 1886, [ii], **35**, 323) and Tollens (Ber. 1886, **19**, 2135; Annalen, 1888, **243**, 335) discovered the catalytic activity of copper in the form of wire gauze. In a typical experiment, air was bubbled through methanol maintained at 40–50°C. and the resulting mixture was passed over a spool of copper wire gauze, 5 cm. long, and heated to a moderate temperature, the products being collected in receivers maintained at 100°C. and about 0°C. respectively.

The first patented method of oxidising methanol catalytically to formaldehyde is that of Trillat (F.P. 199919, 1889; G.P. 55176, 1889) who proposed the use of such catalysts as platinised asbestos, copper oxide, retort carbon, porcelain, etc. On the other hand, the first industrial production of formaldehyde is said to have been established near Hanover in 1889 by the firm of Mercklin and Lösekann, employing a process in which the catalyst was copper wire. About the same time Klar and Schulze (G.P. 106495, 1898; F.P. 288957, 1899) recognised the importance of controlling the ratio of air to methanol in the reacting gases and proposed to carburet air with methanol in a countercurrent scrubbing tower maintained at 40–50°C. By regulating the flow of alcohol and air to the scrubber, the ratio of reactants could be varied at will and, in order to moderate the reaction, it was proposed to dilute the ingoing air with nitrogen derived from the waste gases. The disclosures of Klar and Schulze relate only to the preparation of the reaction mixture and do not refer to any definite type of contact materials.

The formaldehyde industry underwent a rapid development in the decade 1898 to 1908, during which time the most varied types of catalyst were employed, although copper wire gauze was probably the most popular. Morel (J. Pharm. Chem. 1905, **21**, 177) described the catalyst chamber used in a French factory in 1905, which consisted of a metal cylinder fitted with numerous copper tubes containing copper contacts. A plant designed by Orloff (J. Russ. Phys. Chem. Soc. 1908, **40**, 796) and capable of oxidising 17·5 kg. per hour of methanol consisted of a tubular vessel set at an angle of about 10° and containing 169 copper tubes of 19 mm. internal diameter, 2 mm. thickness and 800 mm. length arranged in two concentric circles between two end plates. Glass tubes, 16 mm. internal diameter, 1·25 mm. thick and 120 mm. long, placed in the copper tubes carried the copper contacts which consisted of copper gauze spools about 120 mm. long. Orloff perfected an ingenious device, still employed to some extent, for initiating the reaction without external application of heat. This was effected by placing at the inlet end of the catalyst chamber "ignition pills" prepared by soaking pieces of pumice in a solution of platinum and palladium chlorides and calcining the product. This catalyst, by virtue of its activity at low temperatures, was able to initiate the oxidation and thus to raise the main copper catalyst to the reaction-temperature.

A great advance was made in 1908 when Blank (G.P. 228697, 1908) found that silver was superior to other contacts and gave yields 10–15% greater than those attained with the usual copper catalysts. Since that time a large number of modifications of silver and numerous other catalysts have been described (*vide infra*) but silver gauze is still used almost exclusively in large-scale practice.

The following is a summary of scientific and technical literature with special reference to modern industrial practice.

(1) *Purity of Raw Materials.*

The purity of the air used in the oxidation process is of the utmost importance since catalyst poisoning is very liable to occur. The air should be free from dust particles, sulphur dioxide, hydrochloric acid, hydrogen sulphide and sulphuric acid. Klar (Chem.-Ztg. 1935, **59**, 741) has recorded an instance of catalyst poisoning in a plant located on the coast for which salt in the air was responsible. Silver catalysts in mesh form are said to be more resistant to poisoning than supported silver catalysts. According to Siegl (*ibid.* 1927, **51**, 782) copper catalysts tend to become inactivated by the presence in air of halogen compounds, particularly organic chlorine compounds, even if present in such small amounts as to evade detection by the usual analytical methods. Air purification is best effected by passage through active charcoal or by scrubbing with water or methanol in the presence of alkalis or alkali carbonates.

The methanol used in the process must be free from all volatile organic, or inorganic, sulphur, halogen and cyanogen compounds, while the presence of iron carbonyl in synthetic methanol is particularly objectionable. This last impurity may be removed by passage of the methanol vapour with air over active charcoal or silica gel contacts (B.A.S.F., G.P. 420442, 1924; B.P. 247050, 1925). Zinc compounds, derived from containers or vaporisers, may also accumulate in the contact zone and lead to serious deterioration of the catalyst. Although the presence of appreciable amounts of acetone and especially of higher-boiling ketones and organic by-products, is regarded as deleterious, Bobrov (J. Russ. Phys. Chem. Soc. 1918, **50**, 130) found that the presence of up to 4% of acetone did not affect the operation of a copper gauze catalyst. According to Orloff, however, the methanol used should not contain more than 2% of acetone or 2% of water, but Thomas (J. Amer. Chem. Soc. 1920, **42**, 867) observed that the presence in the methanol of 1·7% of acetone and 10% of water had no influence on silver catalysts. Although it is probable that the presence of substantial amounts of water vapour in the reacting gases will tend to reduce the catalyst temperature and thus slow up the reaction. Hirchberg (B.P. 199759 and 199760, 1922) claims better control of the catalysis in the presence of copper by the introduction of steam in amounts of $\frac{1}{8}$ to $\frac{1}{24}$ by weight of the methanol used. Where highly concentrated formaldehyde solutions are desired, practically anhydrous methanol may be employed as raw material (I.G. Farbenind. A.G., B.P. 267768, 1926).

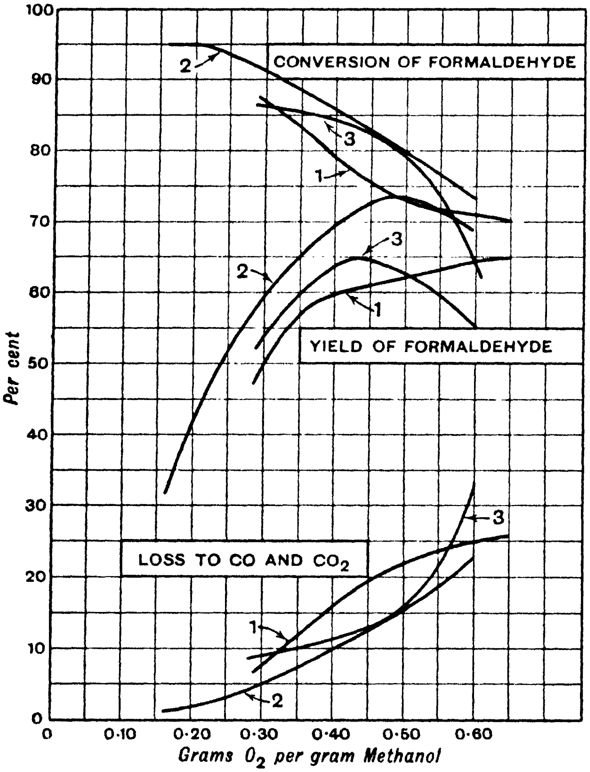


FIG. 1.—OXIDATION OF METHANOL TO FORMALDEHYDE BY AIR.

Curves 1, 2 and 3 refer to experiments with copper, silver and gold-plated catalysts respectively.

(2) *Proportions of Reactants.*

The optimum proportion of air to methanol in the reacting gases varies somewhat with the catalysts but is generally rather less than that required by the equation

$$CH_3{\cdot}OH+\tfrac{1}{2}O_2=CH_2O+H_2O.$$

At oxygen concentrations below the optimum, efficiencies of formaldehyde production are high, but conversions per passage are low, while at concentrations of oxygen in excess of the optimum, conversions fall again while the efficiency of formaldehyde formation also declines on account of increasing production of oxides of carbon. The general effect of varying oxygen concentration on the yields (*i.e.* conversions per pass) and efficiencies in the presence of copper, silver and gold-plated copper catalysts is shown by the experimental data of Thomas as illustrated in Fig. 1 (from Marek and Hahn, " The Catalytic Oxidation of Organic Compounds on the Vapour Phase," 1932, Chemical Catalog Co. Inc., N.Y.). From these results it appears that an oxygen concentration equivalent to 0·45–0·5 g. per g. of methanol is suitable with a silver catalyst. Using gauzes of copper and silver, 80–90 mm. in length, Le Blanc and Plaschke found optimum oxygen proportions of 0·39 g. and 0·46 g. respectively per 1 g. of methanol. On the other hand, Gurewitsch and Tschirwinskaja (J. Gen. Chem. Russ. 1935, **12**, 57) found that, in the presence of copper gauze as catalyst, the best proportion of oxygen was only 50–54% of that required by the above equation, while Natta and Strada (Giorn. Chem. Ind. Appl. 1932, **14**, 545, 551) suggest adding only sufficient oxygen to supply the requisite heat and maintain the reaction without external supply or abstraction of heat. The actual air to methanol proportions used industrially probably vary but, in general, methanol is always in excess. According to Klar, excess of methanol is used to dissipate heat so that a typical crude condensate from the oxidation process may contain 30–36% formaldehyde, 20–24% water and 40–50% unchanged methanol. Satisfactory operation is said by Siegl to produce an exit gas (after condensation and washing) containing, in addition to hydrogen, 3·5–4% of carbon dioxide, very little carbon monoxide and no methanol.

(3) *Catalysts.*

The earlier workers employed catalysts of platinum and palladium, either alone or on carriers such as asbestos. Ruthenium has been suggested as a catalyst (Badische Anilin- u. Soda-Fabrik, G.P. 275518, 1913). Subsequent work has shown, however, that the platinum metals tend to promote further decomposition of the formaldehyde and are thus inferior to silver and copper. Best results were obtained by Orloff with a catalyst of reduced copper on asbestos, impregnated with lower oxides of vanadium. Although Le Blanc and Plaschke found that the catalytic effect of silver was not appreciably better than that of copper, the superiority of silver, first claimed by Blank (G.P. 228697, 1908) has been confirmed by Fokin (J. Russ. Phys. Chem. Soc. 1913, **45**, 268) and especially by Thomas (*l.c.*). Later Kadowaki and Yamada (Rept. Osaka Imp. Univ. Res. Lab. Japan, 1931, **11**, No. 19) found that the catalytic activity of silver is slightly increased by the addition of vanadium or selenium and somewhat depressed by iron, cobalt, chromium, copper, zinc or aluminium. With cylindrical rolls of silver wire, 15 mm. in diameter and 2–6 cm. in length, formaldehyde yields of about 79% were obtained with an oxygen to methanol ratio corresponding to 0·38 to 0·48 g. per g. of methanol.

Copper catalysts, both in the form of gauze (Barbet, B.P. 206158, 1922; U.S.P. 1661063, 1928; Danneel, G.P. Appl. E. 22953, 1918) and also on porous carriers (Enderli, G.P. 318402, 1917; Snelling, U.S.P. 1122811, 1914) have been proposed. Copper vanadate precipitated on carborundum or other carbide of the metals of Group IV is claimed by the Selden Co. (U.S.P. 1930716, 1932) while Clancy (B.P. 163046, 1920, Assr. to Nitrogen Corp.) disclosed the use of an active catalyst prepared by ignition of copper cyanide.

Silver catalysts of the most varied types have been described and the following may be mentioned. Silver precipitated on asbestos (Blank, *l.c.*); finely-divided silver (Bouhard, F.P. 412501, 1910; Kusnezow, U.S.P. 1067665, 1913); metal couples in mechanical combination, *i.e.* unalloyed, such as silver plus 0·01% of platinum in a copper tube (von Hochstetter and Holzverkohlungs-Ind. A.-G., G.P. 402849, 1914); silver vanadate precipitated on diatomaceous earth (Selden Co., U.S.P. 1935054, 1933); electrolytic silver crystals with, or without, the addition of 1 to 10% of difficulty reducible oxides such as the oxides of tungsten, thorium, vanadium, cerium, molybdenum, zinc, aluminium and chromium (E.I. Du Pont de Nemours & Co., U.S.P. 1968552, 1930 and 2005645, 1930); silver prepared by ignition of silver cyanamide (Clancy, B.P. 163046, 1920).

According to Adkins and Peterson (J. Amer. Chem. Soc. 1931, **53**, 1512) molybdic anhydride dispersed on small iron spheres is a highly efficient catalyst for the production of formaldehyde although the optimum conversions per passage are relatively low. However, with a catalyst consisting of the oxides of iron and molybdenum in equal atomic proportions, conversions of 90% and efficiencies of upwards of 91% were attained. The use of catalysts containing at least 40% of molybdenum oxide admixed with one or more oxides of vanadium, iron, lanthanum, thorium, neodymium, zinc or tin has been proposed (Bakelite Corp., B.P. 381570, 1931; U.S.P. 1913404–5, 1931; G.P. 575596, 1930), a specially valuable mixture consisting of 45–50% MoO_3, 45–40% V_2O_5 and 10% FeO.

It has been claimed (Bailey and Craver Assr. to Barrett Co., B.P. 163980, 1920; U.S.P. 1383059, 1921; Canad. P. 228038, 1923; F.P. 533900, 1920; Blom, G.P. 292365, 1913) that vanadium pentoxide is an active catalyst for the production of formaldehyde at temperatures as low as 225°C., so that a large excess of air can be employed with resulting minimised risk of explosion. Furthermore, the presence of water and up to 5% of acetone in the methanol used is stated to have no effect on the activity of this catalyst. However, the efficiency of vanadium pentoxide is said to be increased by admixture with certain other metal oxides, such as those of potassium and manganese (Weiss and Downs, U.S.P. 1851754, 1928; International Aniline and Chem. Co., U.S.P. 2065394).

Other catalysts suggested for this oxidation are incandescent carbon (Kala S.A., F.P. 620754, 1926) and the oxides of cadmium, chromium and manganese (I.G. Farbenind. A.-G., G.P. 441433, 1923). In order to avoid excessive decomposition of the formaldehyde during reaction, it has been proposed to carry out the oxidation in the presence of sufficient ammonia to render the condensed products substantially neutral (Bakelite Corp., U.S.P. 1738745, 1927). Dilution with steam is also suggested as a means of stabilising the formaldehyde and thus increasing the yields (Hirchberg, B.P. 199759 and 199760, 1922).

In modern industrial practice, silver in the form of mesh net is most commonly employed as catalyst. According to Klar, the only alternative catalyst which has so far acquired any technical importance is silver deposited on carriers such as pumice and asbestos. Under suitable working conditions, equally good results are obtainable with both types of catalyst.

(4) *Control of Reaction.*

The oxidation of methanol is a highly exothermic process, the approximate heat effect of the gas phase reaction,

$$CH_3OH+\tfrac{1}{2}O_2=CH_2O+H_2O,$$

being +35·3 kg. cals. per mol. (Kharasch, Bur. Stand. J. Res. 1929, **2**, 359). In the industrial process, part of the heat of oxidation is consumed in promoting the endothermic dehydrogenation, a portion is lost by radiation and part is eliminated as sensible heat of the gaseous products. In general, the dissipation of the surplus heat cannot be effected by radiation or external cooling agencies, so that the catalyst mass is raised to a relatively high temperature. Temperatures of 500–600°C. are maintained in the catalyst zone and control of the temperature is effected partly by regulating the velocity of the gases and, in many cases, by employing an excess of methanol or diluting the reaction mixture with hydrogen (Klar, Chem.-Ztg. 1935, **59**, 741). The hottest part of the catalyst mass is that located near the inlet end, the rear section of the catalyst serving to equalise and control the temperature. While it has been maintained by several investigators that some decomposition of formaldehyde, with consequent reduction in efficiency, is liable to occur if the length of the catalyst zone is increased beyond a certain optimum, Thomas found no evidence for this when using silver or copper gauze contacts. With gold catalysts, however, the loss of formaldehyde by decomposition increased slightly with increasing length, the oxidation being apparently complete in the first 20 mm. of length. The heat-conducting properties of the catalyst are also of some importance and Faith and Keyes (Ind. Eng. Chem. 1931, **23**, 1250) have found that catalysts having the highest coefficient of heat transfer give the best yields of intermediate oxidation products. According to Bobrov, relatively short copper gauze discs, packed perpendicularly to the tube axis, give better results than copper gauze spirals.

As might be anticipated, gas speeds are of considerable importance and fluctuations in feed rate can cause erratic operation when insufficient catalyst mass is used, owing to temperature variations. Linear gas velocities of the order of 1–2 ft. per sec. were used by Thomas, who found, however, that the efficiency of silver gauze catalysts is little affected by relatively large variations in gas speed.

In industrial practice the catalysts are usually gauze mesh of 35–300 mm. diameter (50 mm. diameter and 100 mm. long is typical), placed in a series of copper or silver-plated copper tubes of approximately the same internal diameter. An apparatus described by Schwyzer (Pharm. Ztg. 1930, **75**, 28, 45) consisted of an annular cast-iron vessel provided with a central conduct to facilitate heat dissipation, the catalyst being a bed of copper turnings placed in the annular chamber, which was provided with an external removable electric heater to initiate the reaction. Special apparatus and means for controlling the course of the catalyses have been disclosed by the following patentees: Boake, Roberts & Co., B.P. 110787, 1916; Calvert, B.P. 814, 1915; U.S.P. 1213740, 1917; Brutzkus, B.P. 217747, 1923; Barbet, B.P. 206158, 1922; I.G. Farbenind. A.-G., B.P. 293203, 1927.

(5) *Treatment of Reaction Products.*

The crude reaction product, on condensation, furnishes a crude condensate rich in formaldehyde and a gas which still contains appreciable amounts of methanol vapour. The latter can be removed by countercurrent scrubbing with water, the methanol being subsequently recovered for re-use by fractionation of the aqueous wash liquor. The crude formaldehyde condensate which may, for example, contain 30–36% of formaldehyde, 20–24% of water and a residue of methanol, is usually diluted with aqueous wash liquor and stripped of a part of its methanol content by fractionation in a copper still from which pure methanol is withdrawn as an overhead product and strong formaldehyde solution from the bottom.

Another method of operation consists in subjecting the crude reaction products to a continuous rectification in a column apparatus. In this way it is possible to recover from the bottom plate a non-polymerising solution of formaldehyde free from methylal and containing only 0·1–0·2% of methanol (Hirchberg, B.P. 199759, 1922; Roessler and Hasslacher Chem. Co., U.S.P. 1871019, 1930). Rapid cooling of the hot reaction gases is said to be advantageous and this may be effected by immediately contacting them with a cold aqueous formaldehyde solution (I.G. Farbenind. A.-G., B.P. 260908; Ahlbeck and Bakelite Corp., U.S.P. 1744295, 1927). Very concentrated formaldehyde solutions, or paraformaldehyde, are obtained by oxidising substantially anhydrous methanol, rapidly cooling the reaction products and subjecting the cooled products to a countercurrent washing with a strong solution of formaldehyde (I.G. Farbenind. A.-G., B.P. 267768 and 296847).

Klar has described a third method of treating the reaction products in which the hot mixture of methanol vapour, formaldehyde, steam, nitrogen, hydrogen and oxides of carbon is passed into a series of aluminium columns, in the first of which formaldehyde solution condenses while, at a further point in the system, the bulk of the methanol is recovered for re-use in the process.

(6) *Yields.*

From 100 parts by weight of anhydrous methanol, a yield of 93·75 parts of 100% formaldehyde, or 257 parts by weight of a 36·5% *w/w* solution, can theoretically be obtained. In large scale practice, yields of 88–90% of the theoretical can only be obtained under the most favourable operating conditions, although slightly better results have been reported in laboratory experiments conducted for relatively short periods of time.

(7) *Complete Plant.*

A typical modern plant for the oxidation of methanol to formaldehyde is shown in Fig. 2 Vannino and Seitter, "Der Formaldehyd," Vienna and Leipzig, 1927; *see also* description in Chem. Rundschau für Mitteleuropa u. Balkan, 1925, p. 269). Air is aspirated by the compressor, 1, into a constant pressure receiver, 2, from which it passes into a saturator vessel, 4, where it is preheated and meets a preheated steam of methanol from feeder 3. The resulting mixture of air and methanol vapour passes to a reactor, 5, usually consisting of a bunch of copper tubes charged with the catalyst. Copper tubes, 600 mm. long and 50 mm. internal diameter, charged with silver gauze contacts 110 mm. long and about 50 mm. external diameter, are typical, while an ignition pill is often used to initiate reaction. The products of reaction pass into a separator, 6, from the bottom of which commercial formaldehyde solution is withdrawn.

The bulk of the uncharged methanol is carried over with inert gas and is condensed by means of cooler, 7, and collected in receiver, 12. The uncondensed gas then passes to scrubber, 9, where the residual methanol is removed by countercurrent extraction with water, the resulting dilute methanol being concentrated in column 10 and returned to 12 for re-use.

Production of Formaldehyde by Oxidation of Hydrocarbons.

It has long been known that formaldehyde is produced in small amounts by the incomplete oxidation in the vapour phase of various hydrocarbons. On account of its cheapness and abundance, methane appears particularly attractive as a raw material for such a process. However, despite a voluminous patent and scientific literature, so far little formaldehyde seems to have been produced industrially either from methane or other hydrocarbon gases. It has been stated that considerable quantities of formaldehyde and methanol are produced by catalytic oxidation of natural gas (Ind. Eng. Chem. 1928, **20**, 342), and also as a by-product of the production of carbon black from natural gas (Egloff and Schaad, Chem. Reviews, 1929, **6**, No. 1), while small-scale plant for the production of formaldehyde from methane have been operated in Russia (Chem. Trade J. 1935, **96**, 200; 1937, **100**, 234) and in Germany (Ind. Eng. Chem. News Edit. 1936, **14**, 449).

The general course of the vapour phase oxidation of methane by air or oxygen was elucidated mainly by the scientific work of Bone and his collaborators (J.C.S. 1902, **81**, 535; 1903, **83**, 1074; 1906, **89**, 674) and of Blair and Wheeler (J.S.C.I. 1923, **42**, 81T). Their results indicated that, owing to the instability of formaldehyde, the conditions favouring its formation include operation at relatively low temperatures and for short contact times. For practical purposes this implies that high efficiencies of formaldehyde production can only be attained under conditions of small percentage decomposition per pass, so that multi-stage operation or recycling becomes necessary. By the non-catalytic oxidation of gas mixtures containing 80% methane and 20% oxygen at 665°C., Blair and Wheeler obtained formaldehyde with an efficiency of 65% at very low conversions per pass, so that the actual concentration of formaldehyde in the exit gases was small. Higher concentrations can only be attained under conditions of relatively low efficiency. The highest formaldehyde concentration was obtained by Tropsch and Roelen (Brennstoff-Chem. 1924, **5**, 37) by passing equimolecular mixtures of methane and oxygen through small bore tubes at 1,000°C., when the yield of formaldehyde was 5·96% of the methane entering the system: Ledbury and Blair (Chem. Res. Rep. No. 1, D.S.I.R. 1927) studied the non-catalytic oxidation of methane to formaldehyde in a circulation apparatus. Using a mixture of 80% CH_4 and 20% O_2 with a contact time of about 1 second, at about 700°C. formaldehyde was obtained in a concentration of 2mg. per litre of gas mixture and an estimated yield of 30%, calculated on the methane consumed.

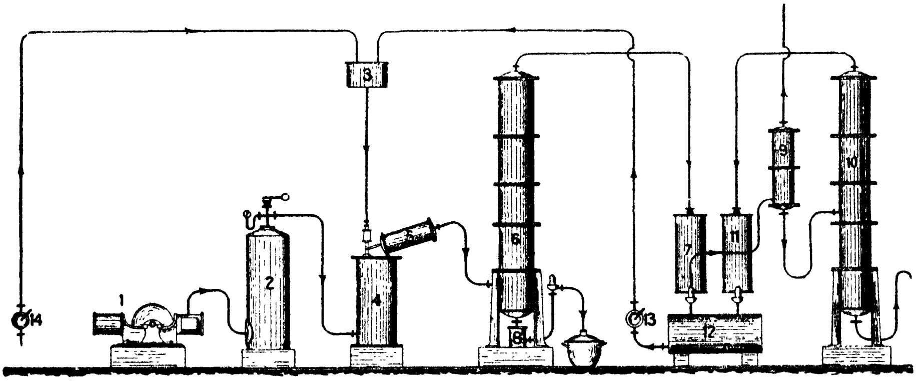


Fig. 2.

The catalytic oxidation of methane to formaldehyde has been the subject of a large number of scientific studies and patent disclosures, which are reviewed by Roelen (Ges. Abh. Kennt. Kohle, 1925, **7**, 111), Egloff and Schaad (Chem. Reviews, 1929, **6**, No. 1), Marek and Hahn ("Catalytic Oxidation of Organic Compounds in the Vapour Phase," 1932) and Mayor (Rev. Chim. Ind. 1927, **46**, 70, 110). Interesting results were obtained by Medvedev (Trans. Karpov Inst. Chem. 1924, No. 3, 54; 1925, No. 4, 117) using catalysts consisting of phosphates of lead, aluminium, tin and iron activated by the addition of about 0·13% of hydrogen chloride in the gas mixture used, and operating at 500–700°C. With mixtures of methane and air, or oxygen, one pass operation furnished formaldehyde in yields of 5–6% based on the methane passed through the apparatus. Schönfelder (Ber. Ges. Kohlentech. 1923, **4**, 247) found that by passage of mixtures of methane, steam and air over copper or silver catalysts at 500°C., 55–58% of the hydrocarbon was oxidised to formaldehyde, 10–20% to carbon monoxide and 25–40% remained unchanged. Oxidation of methane with an equal volume of air at 550° in contact for 1 second with a suitable catalyst is claimed by James (U.S.P. 1588836, 1926) to yield formaldehyde in amounts corresponding to 6·75% of the methane treated. Oxides of nitrogen have been found to exert a distinct catalytic influence on the oxidation of methane to formaldehyde (Layng and Soukup, Ind. Eng. Chem. 1928, **20**, 1052; Frolich, Harrington and Waitt, J. Amer. Chem. Soc. 1928, **50**, 3216), and Bibb (U.S.P. 1392886, 1921; 1547725, 1925) has obtained a yield of 123 g. of formaldehyde per cubic meter of gas used by oxidising natural gas in the presence of this catalyst at 730°C.

The homologues of methane appear to furnish higher proportions of formaldehyde by partial oxidation than does methane itself, probably because of the lower temperatures and shorter contact times involved. By heating a mixture of ethane and air (2 vol.) at 700°C. for about 1 second and recycling part of the reaction products, yields of formaldehyde amounting to about 7·4% of the theoretical have been obtained (Curme, U.S.P. 1729711, 1929, Assr. to Carbide and Carbon Chemicals Corp., *also* B.P. 238938, 1924).

The industrial possibilities of the non-catalytic oxidation of ethylene to formaldehyde have been explored by Ledbury and Blair (*l.c.*), who obtained best results by passing a mixture of 15–20% ethylene and a residue of air through a tubular reactor at 575°C. and a contact time of about 1 second. Under these conditions, formaldehyde can be obtained with an efficiency of 50–75% but the conversions per pass (and also the concentration of formaldehyde in the exit gas) are low, so that repeated recycling becomes necessary.

The oxidation of hydrocarbons by means of ozone and also by air under the influence of the silent electric discharge has been studied but neither method is of industrial importance.

PRODUCTION OF FORMALDEHYDE BY HYDROGENATION OF OXIDES OF CARBON.

The hydrogenation of carbon monoxide to formaldehyde according to the reversible equation $CO+H_2 \rightleftharpoons CH_2O$ represents an intermediate stage in the well-known synthesis of methanol, and it might be expected, therefore, that such a synthesis would be of technical value. In practice, however, it is difficult to stop the hydrogenation at the desired stage and no industrial applications of this reaction have been recorded. Despite several patent claims (*e.g.* Dreyfus, B.P. 108855 and 157047, 1917; Church, F.P. 519649, 1919; Lush, B.P. 180016, 1921; Françon, B.P. 450449, 1935) only traces of formaldehyde are obtainable at atmospheric pressure (Jaeger and Winkelmann, Ges. Abh. Kennt. Kohle, 1925, **7**, 55). Somewhat better results appear possible at elevated pressures and E. M. Botscharova and B. M. Dolgov (J. Gen. Chem. Russ. 1934, **4**, 145) obtained a 6% yield of formaldehyde from water gas at 125 atmospheres pressure and 400°C. in the presence of a $4MgO-Mn_2O_3$ catalyst. A variety of catalysts have been claimed for the high-pressure synthesis of formaldehyde (Soc. Chim. Grande Paroisse, B.P. 272155, 1927; Arsem and Commercial Solvents Corp. U.S.P. 1740141, 1929; Selden Co., U.S.P. 1824896, 1925). The reduction of carbon monoxide by hydrogen at sub-atmospheric pressures and under the influence of anodic light yields formaldehyde (Usines de Melle, B.P. 469371, 1937) while Roman (B.P. 371377, 1932) has disclosed a catalytic process at atmospheric pressure in which a multi-metal catalyst is used and revivified at very frequent intervals. Reviews of this subject have been contributed by Küster (Brennstoff-Chem. 1936, **17**, 103) and Neumann and Biljcevic (Z. angew. Chem. 1927, **40**, 1469).

MISCELLANEOUS METHODS OF PREPARATION.

The oxidation of acetaldehyde in the vapour phase is claimed to furnish formaldehyde in yields of 50% or thereabouts (Consortium f. Elektrochem. Ind., B.P. 178842, 1922; U.S.P. 1864541) while methylamine may also be oxidised to formaldehyde (Trumpler, Swiss P. 111120, 1924). Passage of dimethyl ether and air over a copper or silver catalyst at elevated temperatures has also been proposed (Meister, Lucius and Brüning, G.P. 413448).

Processes for the production of formaldehyde by catalytic reduction of formic acid (Arsem and Commercial Solvents Corp., U.S.P. 1648602; B.A.S.F., G.P. 185932; Goldschmidt, G.P. 183856) or by decomposition of various formates (Hofmann, G.P. 316217; Guignard, F.P. 550380) are scarcely attractive in view of the cost of the raw materials.

The hydrolysis of methylene dichloride by means of water (Rhenania Ver. Chem. Fabrik., G.P. 362746), or by steam in the presence of alkaline salts, furnishes good yields of formaldehyde (Meister, Lucius and Brüning, G.P. 382391). Hydrolysis can also be effected in the vapour phase over activated charcoal at 260–270°C., when an 84% yield of formaldehyde is obtainable (I.G. Farbenind. A.G., G.P. 426670; B.P. 189432, 1922). Various methods of producing hexamethylenetetramine and allied products by reacting methylene dichloride with ammonia, aqueous ammonia or ammonium chloride have been proposed (Karpen, B.P. 230015; U.S.P. 1499001, 1499002, 1568817, 1568823, 1630782; Holzverkohlungs Ind., B.P. 195602, 1922), but no large-scale applications of these processes have been recorded.

MONOMERIC FORMALDEHYDE.

Formaldehyde was first obtained in relatively pure form by Kekulé (Ber. 1892, **25**, 2435; *see also* Sachs, Ber. 1899, **31**, 1231) by heating paraformaldehyde. Walker (J. Amer. Chem. Soc. 1933, **55**, 2821) prepared this substance by distillation of an alkali-precipitated polyoxymethylene. The monomer exhibits a marked tendency to undergo polymerisation, particularly in the presence of traces of water and oxygen. Recently, Spence and Wild (J.C.S. 1935, 338) have prepared more stable specimens of the liquid monomer by depolymerisation of paraformaldehyde and separation of water in a series of cooled traps. Anhydrous formaldehyde gas is stable at 80–100°C. at which temperature it shows little deviation from the gas laws. The gas at room temperature is quite soluble in methanol and very soluble in water. Gaseous formaldehyde decomposes at temperatures above 500°C., mainly into carbon monoxide and hydrogen (Bone and Smith, J.C.S. 1905, **87**, 910), this reaction being accelerated by numerous catalysts (Müller, Ber. 1921, **54** [B], 3214; Tropsch, Otto and Roelen, Abh. Kennt. Kohle, 1925, **7**, 15, 25; Medvedev and Robinson, Trans. Karpov Inst. Chem., 1925, **4**, 117).

The following physical constants have been recorded:

Liquid monomer, b.p. −21°C. (Kekulé, *l.c.*); −19·2° at 760 mm. (Spence and Wild, J.C.S. 1935, 507); m.p. −92°C. (Harries, Ber. 1901, **34**, 635); −118°C. (Spence and Wild, *l.c.*; latent heat of vaporisation, 5,160 g.-cal./mol. (Mali and Ghosh, J. Indian Chem. Soc. 1924, **1**, 37); 5,570 g.-cal./mol. (Spence and Wild, *l.c.*); density, 0·8153 at −20°C. (Kekulé); vapour pressure-temperature relationship

$$\log_{10} p\text{atm.} = -1429/T + 1{\cdot}75 \log T - 0{\cdot}0063T + 3{\cdot}0177$$

(Spence and Wild, *l.c.*).

Gaseous monomer.—Heat of formation, 25,400 g.-cal. (Délépine, Ann. chim. phys. 1898, [vii], **15**, 554; Compt. rend. 1897, **124**, 1525); heat of formation at constant volume, 27,800 g.-cal. (von Wartenberg, Muchlinski and Riedler, Z. angew. Chem. 1924, **37**, 457; von Wartenberg, *ibid.* 1925, **38**, 591); heat of solution in water, 15,400 g.-cal. (Délépine).

AQUEOUS SOLUTIONS OF FORMALDEHYDE.

Formaldehyde is available commercially in the form of its aqueous solutions, which always contain appreciable amounts (7–13%) of methanol to prevent the deposition of water-insoluble polymers. The 40% formaldehyde of commerce contains 36–38% by weight of formaldehyde; the product required by the British Pharmacopœia should contain 36–38 g. per 100 c.c. and have a sp.gr. of 1·080. To inhibit the formation of polymers, it has been proposed to add substances such as sodium soaps (Hirchberg, B.P. 211943, 1922), urea (Canadian Industries, Ltd., Canad. P. 341481, 1933), hydrogen sulphide (Du Pont de Nemours & Co., B.P. 427423, 1933; U.S.P. 2002243, 1932) and water-soluble nitrogen compounds such as thiourea (Du Pont de Nemours & Co., B.P. 428871, 1933). The addition of 10–15% of glycerol and sufficient alkali to give a distinctly alkaline reaction is also claimed as a method of stabilising concentrated aqueous solutions (International Chem. Co., F.P. 544293). Formaldehyde solutions for pharmaceutical purposes are prepared by distillation in copper stills with addition of lime to the distillate in order to neutralise formic acid.

The following values of d_4^{18} for methanol-free formaldehyde solutions are given by von Wartenberg and Lerner-Steinberg (Z. angew. Chem. 1925, **38**, 591).

d_4^{18}.	g. CH_2O per 100 g.	g. CH_2O per 100 cc.
1·000	0·5	0·5
1·010	3·7	3·8
1·020	7·0	7·1
1·030	10·2	10·5
1·040	13·4	14·0
1·050	16·7	17·5
1·060	19·8	21·0
1·070	23·0	24·6
1·080	26·2	28·3
1·085	27·8	30·1
1·090	29·3	32·0
1·095	30·9	33·8
1·100	32·5	35·7
1·105	34·0	37·6
1·110	35·6	39·5
1·115	37·2	41·4
1·120	38·7	43·4
1·125	40·3	45·3

The presence of methanol considerably reduces the density of formaldehyde solutions, as may be seen from the following figures (data quoted by Ullmann, "Enzyklopädie der technischen Chemie, 1930, vol. 5; *see also* Maue, Pharm. Ztg. 1918, **63**, 197; Gradenwitz, *ibid.* 241).

VALUES OF d_{15}^{15}.

Methanol %.	Formaldehyde, %.					
	30	32	34	36	38	40
0	1·0940	1·1003	1·1066	1·1128	—	—
2	1·0892	1·0953	1·1015	1·1077	—	—
4	1·0847	1·0908	1·0969	1·1030	—	—
6	1·0799	1·0860	1·0921	1·0983	1·1045	—
8	1·0755	1·0815	1·0875	1·0935	1·0996	1·1058
10	1·0711	1·0770	1·0829	1·0888	1·0947	1·1006
12	1·0664	1·0721	1·0779	1·0836	1·0894	1·0952
14	1·0618	1·0674	1·0730	1·0787	1·0843	1·0899
16	1·0573	1·0628	1·0684	1·0740	1·0796	1·0852
18	1·0527	1·0580	1·0635	1·0691	1·0747	—
20	1·0481	1·0534	1·0587	1·0641	1·0695	—

The heat of solution of formaldehyde in water is 15,400 g.-cal. per mol. (Délépine, *l.c.*), the heat of formation of aqueous formaldehyde being 40,300 g.-cal. (Délépine).

Information on the concentration of formaldehyde solutions by distillation is conflicting. Thus, while Auerbach (Arb. Kais. Gesundh. 1905, **22**, 584) found that the boiling point of aqueous solutions decreased with increasing formaldehyde concentrations up to 30% and then remained practically constant, Gibson and Wilkinson (J. Amer. Chem. Soc. 1921, **43**, 695) concluded that an 8% solution constituted a constant boiling mixture and that distillation of solutions below 8% gave distillates more concentrated than the residual liquid. On the other hand, Ledbury and Blair (*l.c.*) fractionated methanol-free formaldehyde solutions in a 5-section Young column and found that a 30% solution approximates to a constant boiling mixture (b.p. 98·7°C. at 760 mm.); so that it is possible to concentrate formaldehyde in the distillate or in the residue, depending on whether the concentrations of the initial solution are respectively below or above 30%. Quite different results are recorded by Zimmerli (Ind. Eng. Chem. 1927, **19**, 524), who was able to concentrate formaldehyde solutions to yield distillates with a maximum content of 56% of formaldehyde by using an 8 ft. packed column and high reflux ratios. Even weak solutions could be concentrated, leaving a residue entirely free from formaldehyde. Zimmerli believed that the formation of methylene glycol, $CH_2(OH)_2$, was responsible for this fractionation, a 56% formaldehyde (b.p. 99°C.) corresponding to 90% of the hypothetical glycol, the existence of which has also been inferred from physical and chemical evidence.

It has been shown by Korshev and Rossinkaja (J. Chem. Ind. Russ. 1935, **12**, 610, 721) that formaldehyde can be concentrated by distillation under reduced pressure, the distillate vapours being much poorer in formaldehyde than under atmospheric pressure. Thus, the vapours evolved on distillation of 7%, 17% and 28% aqueous formaldehyde solutions at 21 mm. contain 0·46%, 1·41% and 4·60% of formaldehyde respectively while the corresponding concentrations for distillation at 1 atmosphere are 6·95, 14·96 and 22·8%. The addition of calcium chloride in atmospheric pressure distillation increases the concentration of formaldehyde in the vapours so that a 13% aqueous formaldehyde can be made to yield directly a distillate containing 37% of formaldehyde. For the concentration of very dilute solutions, it is proposed to remove part of the water by distillation at 32°C. and 30 mm. and then distil the residue with the addition of calcium chloride to furnish a distillate containing 37% formaldehyde.

Reduction in free acidity to below 0·01% by weight, calculated as formic acid, followed by concentration under reduced pressure, has been proposed (Deuts. Gold- u. Silber-Scheideanstalt, vorm Roessler, B.P. 447050, 1936). Smith (U.S.P. 2015180) obtains concentrated formaldehyde solutions by distilling aqueous formaldehyde with substances, such as calcium chloride, which raise the boiling-point of the solution above the decomposition point of the formaldehyde polymers, and collecting the first fractions. With a view to decomposing polymeric forms and thus increasing the formaldehyde concentration in the vapour phase, distillation under increased pressures has been advocated, particularly in the presence of a salt or an acid or acidic salt (Deuts. Gold- u. Silber-Scheideanstalt vorm Roessler, B.P. 471762, 1937; Roessler and Hasslacher, Chem. Co., U.S.P. 1905033, 1933). Ledbury and Blair have found that pressure distillation in the presence of iron, monel metal and lead involves considerable decomposition of formaldehyde in aqueous solutions, but nickel, aluminium and copper are less objectionable in this respect.

The partial pressures of formaldehyde in aqueous solutions of 5–40% concentrations and at temperatures of 0–45°C. have been determined by Ledbury and Blair, using a dynamic method. The presence of methanol increases the partial pressures of formaldehyde in this range of concentration and temperature. According to Walker (J. Physical Chem. 1931, **35**, 1104) the partial pressure of formaldehyde is much less than would be expected on the basis of Henry's law and appears to be proportional to the concentration of methylene glycol.

Chemical evidence, already referred to, of the existence of hydrated forms of formaldehyde in aqueous solution is supported by a number of physico-chemical data including cryoscopic molecular weight measurements, Raman spectra and absorption spectra. In dilute aqueous solutions, formaldehyde exists apparently almost entirely in the form of methylene glycol but in more concentrated solutions, this monohydrate is in equilibrium with other hydrates such as

$$(CH_2O)_3\cdot H_2O \text{ or}$$
$$HO\cdot CH_2\cdot O\cdot CH_2\cdot O\cdot CH_2\cdot OH.$$

According to Auerbach and Barschall (Arb. Kais. Gesundh. Amt. 1905, **22**, 584) methylene glycol and trimethyleneglycol are the only hydrates present in solutions containing up to 34% formaldehyde. Higher polymerised hydrates, or hydrated polymers, are formed very readily from more concentrated solutions and tend to be precipitated in solid form. When a concentrated formaldehyde solution is diluted with water, the polymerised hydrates dissociate into methylene glycol but equilibrium is only obtained after several hours at room temperature (Walker, Ind. Eng. Chem. 1931, **23**, 1220).

POLYMERS OF FORMALDEHYDE.

Two entirely different types of formaldehyde polymers must be distinguished, namely (i) true polymers of the general formula $(CH_2O)_n$ and (ii) hydrated polymers of the type $(CH_2O)_n\cdot H_2O$, most of which have the constitution of polymethyleneglycols, namely,

$$HO\cdot CH_2\cdot [O\cdot CH_2]_n\cdot OH.$$

Only substances of the second type are of industrial importance.

Paraformaldehyde, a substance of considerable technical importance, consists of a mixture of polymethyleneglycols of the formula

$$(CH_2O)_n\cdot H_2O$$

where n varies between 6 and 50 according to the degree of polymerisation (Staudinger, Annalen, 1929, **474**, 241, 250). It is a white amorphous powder, melting at 120–130°C. (sealed tube) and smelling strongly of formaldehyde, with a formaldehyde content of about 95%. It dissolves slowly in cold water, more rapidly on warming, to yield solutions which tend to be transformed into aqueous formaldehyde; this transformation is said to be very rapid on heating. It is insoluble in alcohol and ether.

Paraformaldehyde is slowly precipitated at ordinary temperatures from formaldehyde solutions of more than 30% strength; at lower temperatures the limiting concentration is lower. Several industrial methods of preparation have been described, the main object being the preparation of a product as soluble in water as possible and free from insoluble polymers. In a method described by Schwyzer (Chem.-Ztg. 1930, 75, 28, 45), aqueous formaldehyde is distilled to the extent of about 60% in an enamelled iron vessel and the residue is transferred to a second enamelled vessel where it is agitated for 48 hours at 5–10°C. to yield a solid mass of paraformaldehyde. Patented methods of preparation include evaporation of formaldehyde solutions at low temperatures either under reduced pressure (Richter, F.P. 760075, 1933; Nasch, B.P. 420993, 1932) or by adding substances forming low-boiling azeotropes with water (Deuts. Gold- u. Silber-Scheideanstalt, vorm Roessler, B.P. 375744). Paraformaldehyde is also produced by slowly cooling a 55–65% aqueous formaldehyde solution at a rate of 1–3°C. per hour, preferably in the presence of an electrolyte (Deuts. Gold- u. Silber-Scheideanstalt, vorm Roessler, B.P. 421691, 1933).

α-Polyoxymethylene is a mixture of hydrated polymers similar to paraformaldehyde but having a higher degree of polymerisation, the values of n in the formula $(CH_2O)_n{\cdot}H_2O$ being 100 or over (Staudinger, Annalen, 1929, **474**, 241, 250; Mannich, Ber. 1919, **52** [B], 160). Like paraformaldehyde, it dissolves readily in dilute alkalies and in sodium sulphite solutions. However, it is less soluble in water than paraformaldehyde and has a higher melting-point, *e.g.* 160–168°C. in a sealed tube. On heating in an open tube it is transformed into gaseous formaldehyde without melting, while its aqueous solutions undergo slow depolymerisation to formaldehyde. Solutions of paraformaldehyde and α-polyoxymethylene can be used in place of formaldehyde in most chemical reactions. It is prepared by the action of dehydrating agents on aqueous formaldehyde solutions, *e.g.* by adding 1 vol. of conc. sulphuric acid to 10 vol. of 38% formaldehyde solution. The product is washed with water and, after drying over phosphorus pentoxide, contains about 99% of available formaldehyde (Staudinger, *l.c.*). A similar polymer can be prepared by the action of alkalies, such as sodium or potassium hydroxides, on formaldehyde solutions. By treating a 50–60% aqueous solution of formaldehyde with a few parts per thousand of inorganic or organic basic material such as ammonia, amines or urea, a crystalline product is said to be obtained, which after vacuum drying, contains 0·5–1·5% of combined water (Pirlet, F.P. 765540, 1933). Solid granular polymers are obtained by treating 45% formaldehyde solutions with a small amount of dilute sodium carbonate below 50°C. (I.G. Farbenind. A.-G., B.P. 303258, 1927), or from solutions containing 25%, or less, formaldehyde by addition of sulphuric or phosphoric acids of at least 2% concentration at temperatures below 60°C. (Schilt, B.P. 342668, 1929).

β-Polyoxymethylene is similar to the abovementioned polymers but has probably a higher degree of polymerisation. It is produced by treating 10 vol. of 40% formaldehyde with 4 vol. of concentrated sulphuric acid. The polymer always contains a small amount of sulphuric acid not removed by water washing and probably combined in the form of sulphuric acid derivatives of the higher polymethyleneglycols. It is insoluble in alcohol and ether, slightly soluble in water (3·3% at 18° and 4% at 25°C.), but dissolves in aqueous sodium sulphite. Heating in an open tube converts it partly into gaseous formaldehyde and partly into α-trioxymethylene; in a sealed tube it melts at 163–168°C. (Auerbach).

γ-Polyoxymethylene is produced along with α- and β-polyoxymethylenes by the action of 4 vol. of concentrated sulphuric acid on 10 vol. of formaldehyde solution containing methanol. This substance is not a true polymer of formaldehyde since Staudinger has shown that it contains combined methanol, probably in the form of dimethyl ethers of polymethyleneglycols. In agreement with this structure, γ-polyoxymethylene is scarcely soluble in water and does not dissolve in dilute alkalies or sodium sulphite so that it is readily separated from α- and β-polyoxymethylenes. It melts at 160–168°C. in a sealed tube. By prolonged action of boiling water it is converted into *δ-polyoxymethylene*, a change which is represented by Staudinger as follows:

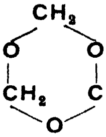
$$CH_3O{\cdot}[CH_2{\cdot}O]_n{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}OCH_3$$
$$\rightarrow CH_3O{\cdot}[CH_2O]_n{\cdot}CH_2{\cdot}CH(OH){\cdot}OCH_3.$$

This δ-polymer is insoluble in water, sodium sulphite solution, alcohol and ether. It melts at 169–170°C. in an open tube without decomposition, but at higher temperatures it yields formaldehyde.

ε-Polyoxymethylene is the name given to an amorphous polymer melting at 195–200°C. and insoluble in water and alkaline solutions. This substance was discovered by Hammick and Boeree (J.C.S. 1922, **121**, 2738) but its constitution is not definitely known. Its composition corresponds with a true polyoxymethylene, *i.e.* with $(CH_2O)_n$, but in its physical properties it bears a closer resemblance to the polymethylene glycols or hydrated polymers.

The true polyoxymethylenes of the formula $(CH_2O)_n$ differ from the hydrated polymers in not containing combined water, methanol or sulphuric acid. On thermal decomposition, the former yield gaseous monomeric formaldehyde, while the latter give partially polymerised vapours. So far, only two members of the true polyoxymethylene type have been described, namely α-trioxymethylene and tetraoxymethlene.

α-Trioxymethylene is obtained in 10% yield by sublimation from a mixture of 10 parts of paraformaldehyde and 1 part of 50% sulphuric acid in an evacuated and sealed tube. It is also produced by subliming β-polyoxymethylene, the sulphuric acid content of which probably acts as a catalyst. The purified compound is a crystalline solid melting at 64°C. with a smell somewhat resembling that of chloroform. It is insoluble in water, aqueous alkaline or sodium sulphite solutions, slightly soluble in light petroleum and soluble in numerous organic solvents. It fails to give the characteristic formaldehyde reactions with Schiff's reagent or ammoniacal silver nitrate and is converted by sulphuryl chloride into chloracetic acid. The vapour of the compound, which is stable up to about 200°C., has a density corresponding to $(CH_2O)_3$. The polymer probably has the cyclic structure.



(Auerbach and Barschall, Arb. Kais, Gesundh. Amt. 1907, **27**, 182; Hammick and Boeree, *l.c.*).

Tetraoxymethylene was obtained by Staudinger and Lüthy (Helv. Chim. Acta, 1925, **8**, 65) by heating an insoluble polyoxymethylene diacetate at 150°C. *in vacuo*. It is a crystalline solid, m.p. 112°, with a vapour density corresponding to a tetramer of formaldehyde, $(CH_2O)_4$.

Chemical Reactions of Formaldehyde.

Oxidation of formaldehyde yields formic acid and its degradation products depending upon the conditions. Treatment of 30% formaldehyde solutions with oxygen in the presence of platinum gives carbon dioxide and water, while sodium hypochlorite oxidises it to formic acid (Dehn, J. Amer. Chem. Soc. 1909, **31**, 1229). In dilute sulphuric acid solution, electrolytic oxidation gives formic acid and oxides of carbon (Law, J. Amer. Chem. Soc. 1905, **87**, 199); in alkaline solution formic acid and hydrogen (Müller, Z. angew. Chem. 1922, **35**, 689) are formed. In aqueous alkaline solution, formaldehyde is oxidised by hydrogen peroxide to yield sodium formate and hydrogen, a reaction which has been made the basis of an accurate quantitative method of estimation (Blank and Finkenbeiner, Ber. 1898, **31**, 2979). Rieche and Meister (*ibid.* 1935, **68** [B], 1465) have shown that in anhydrous media hydrogen peroxide combines with formaldehyde to give hydroxymethyl hydroperoxide, a relatively stable oil.

Formaldehyde is a strong reducing agent and in alkaline solutions can reduce salts of many metals, including the noble metals, mercury, bismuth, iron, osmium, etc., with precipitation of the free element. In strong alkaline solutions of formaldehyde, silver oxide and cuprous oxide catalyse the evolution of hydrogen in accordance with the equation

$$CH_2O+NaOH=H{\cdot}CO_2Na+H_2$$

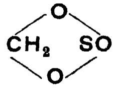
(Vanino, *ibid.* 1903, **36**, 3304).

Even in dilute aqueous solutions, formaldehyde combines with ammonia to yield the monoacid base, *hexamethylenetetramine* in accordance with the equation

$$6CH_2O+4NH_3=N_4(CH_2)_6+6H_2O.$$

This technically important material is a white crystalline solid, soluble in water and alcohol but insoluble in ether. Its production has been made the basis of a titrimetric method of determining formaldehyde (Legler, *ibid.* 1883, **16**, 1933; Loew, J. pr. Chem. 1886, [ii], **33**, 326). Passage of ammonia into a strong, well-cooled, aqueous solution of formaldehyde yields a colourless oil, possibly tri-(hydroxymethyl)-amine, which readily changes to hexamethylene tetramine.

With hydrogen sulphide, formaldehyde yields trimeric thioformaldehyde, (CH_2S). Formaldehyde oxime, b.p. 84–85°C., is readily polymerised to a trimer, $(CH_2{:}NOH)_3$. Fuming sulphuric acid and trioxymethylene give methylene sulphate



(Delépine, Compt. rend. 1899, **129**, 831). With hydrogen chloride a variety of compounds are formed, including *chloromethyl ether*, *dichloromethyl ether*, *monochloromethyl* alcohol and *di-(chloromethoxy)-methane*. The preparation of *fluoromethyl* alcohol from hydrogen fluoride and formaldehyde has been disclosed with a view to its use as a bactericide and fungicide (Meyer, G.P. 443507).

Sodium bisulphite combines with formaldehyde to yield the compound

$$CH_2O{\cdot}NaHSO_3{\cdot}\tfrac{1}{2}H_2O,$$

readily soluble in water and methyl alcohol and less soluble in ethyl alcohol. It is reduced to $(CH_2O)_2{\cdot}Na_2S_2O_4$ ("*Hyraldite*") and sodium formaldehydesulphoxylate,

$$HO{\cdot}CH_2{\cdot}OSONa{\cdot}2H_2O$$

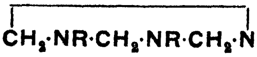
("*Rongalite C*"), both of which are of industrial importance.

Depending upon the experimental conditions, alkaline reagents convert formaldehyde into methyl alcohol and formic acid (Cannizzaro reaction), or into a mixture of hexoses, including α-acrose, as well as intermediate products such as glycollaldehyde and dihydroxyacetone. In general, strong bases and concentrated formaldehyde solutions favour the Cannizzaro reaction while weak bases, such as calcium carbonate or lead oxide, and dilute formaldehyde solutions, yield products of the modified aldol condensation.

Formaldehyde is capable of reacting with almost all types of organic compounds, including hydrocarbons, carbohydrates, aldehydes, ketones, carboxylic acids, esters, alcohols, phenols, amines, hydrocyanic acid, hydrazines, hydroxylamines, urea, nitro-compounds, amides and proteins. In many of these reactions formaldehyde combines with an addendum RH to yield first methylol derivatives, $R{\cdot}CH_2{\cdot}OH$ and then $R{\cdot}CH_2{\cdot}R$. Thus, with acid amides, compounds of the type

$$R{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}OH \text{ and } (R{\cdot}CO{\cdot}NH)_2CH_2$$

are formed. Combination of formaldehyde with primary aliphatic amines gives alkylaminomethanols, $R{\cdot}NH{\cdot}CH_2{\cdot}OH$, which are dehydrated by solid alkalis to $(RN{:}CH_2)_3$, probably having a cyclic structure,



$$CH_2{\cdot}NR{\cdot}CH_2{\cdot}NR{\cdot}CH_2{\cdot}NR.$$

Secondary amines combine by typical reactions to give first $R_2N{\cdot}CH_2{\cdot}OH$ and then $CH_2(NR_2)_2$. Examples of the introduction of the $-CH_2{\cdot}OH$ group into nitrogen bases are the reaction with benzylamine to yield $C_6H_5{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}OH$ (Henry, Bull. Soc. chim. 1895, [iii], **13**, 157) and with carbazole to yield N-methylol carbazole (Lange, G.P. 256757). More complex reactions occur with many aromatic bases. Thus aniline combines with aqueous formaldehyde to yield *anhydroformaldehydeaniline*, $C_6H_5{\cdot}N{:}CH_2$, which exists as a trimer, probably of cyclic structure and also in a higher polymeric form. In the presence of dilute alkali, *dianilinomethane*, $CH_2(NH{\cdot}C_6H_5)_2$, is formed. Both anhydroformaldehydeaniline and dianilinomethane combine with aniline, on heating with aniline hydrochloride to yield mainly 4:4′-diaminodiphenylmethane. Similar reactions occur with *o*-toluidine and *p*-toluidine (Morgan, J.S.C.I. 1930, **49**, 245T). Still more complex reaction products have been isolated from the reaction between formaldehyde and *p*-toluidine (Tröger, J. pr. Chem. 1887, [ii], **36**, 227; Wagner, J. Amer. Chem. Soc. 1935, **57**, 1296). Reaction of formaldehyde with dimethylaniline gives tetramethyl-4:4′-diaminodiphenylmethane, an important dye intermediate. The condensation of formaldehyde with phenols is a reaction of the greatest technical importance in the manufacture of synthetic resins. Condensation in the presence of acidic catalysts yields fusible soluble resins but a number of simple intermediate substances, including hydroxylated diphenylmethanes, have been isolated (Baekeland and Bender, Ind. Eng. Chem., 1925, **17**, 225; Megson and Drummond, J.S.C.I. 1930, **49**, 251T). Alkaline condensing agents favour the production of insoluble resins, but intermediate crystalline substances in which the methylol group has been introduced into the phenolic molecule, such as *o*-hydroxybenzyl alcohol, have been isolated (Lederer and Manasse, Ber. 1894, **27**, 2411; Megson and Drummond *l.c.*).

In its condensation with aldehydes and ketones under the influence of alkaline reagents, resinous products are usually formed, although intermediates can often be isolated. The reaction apparently proceeds by repeated introduction of methylol groups at the carbon atom adjacent to the CO group. Thus, γ-ketobutyl alcohol and bis-hydroxymethyl-tetrahydro-γ-pyrone have been isolated from the products of condensation of formaldehyde and acetone. Under similar circumstances methyl ethyl ketone yields γ-keto-β-methylbutyl alcohol,

$$CH_3{\cdot}CO{\cdot}CH(CH_3){\cdot}CH_2{\cdot}OH,$$

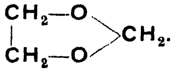
and γ-keto-β-hydroxymethyl-β-methylbutyl alcohol, $CH_3{\cdot}CO{\cdot}C(CH_3){\cdot}(CH_2OH)_2$. (Morgan and Holmes, J.C.S. 1932, 2667; *see also* Décombe, Compt. rend. 1936, **203**, 1077). Condensation of formaldehyde with acetaldehyde in alkaline media yields finally pentaerythritol, $C(CH_2{\cdot}OH)_4$, a substance of importance in the manufacture of explosives. In this reaction, three methylol groups are introduced into the acetaldehyde molecule, with the simultaneous reduction of the aldehyde group. In the presence of potassium bicarbonate, three methylol groups are introduced into the nitromethane molecule to yield, $NO_2{\cdot}C(CH_2{\cdot}OH)_3$.

Formaldehyde can be condensed with aromatic hydrocarbons in the presence of sulphuric acid and in glacial acetic acid solution to yield diarylmethane hydrocarbons (Baeyer, Ber. 1872–74). In the presence of a large proportion of formaldehyde, or its equivalent, insoluble amorphous or resinous solids are formed (Nastukov, J. Russ. Phys. Chem. Soc. 1903, **35**, 824; 1904, **36**, 881; *see also* Ellis, "The Chemistry of Synthetic Resins," 1935, Vol. 1, pp. 263–267). Addition of formaldehyde to unsaturated hydrocarbons in the presence of sulphuric acid as catalyst takes place in accordance with the scheme

$$>C{=}C<+CH_2(OH)_2 \rightarrow >C(CH_2OH){\cdot}C(OH)<$$

1:3-glycols being formed. Thus styrene and formaldehyde in acetic acid solution yield 2-phenyl-1:3-propylene glycol and its methylene ether (Prins, Proc. Acad. Sci. Amsterdam, 1919, **22**, 51). Propylene and formaldehyde similarly give 1:3-butylene glycol.

Like other aldehydes, formaldehyde yields acetals on reaction with alcohols in the presence of acid catalysts. With 1:2- and 1:3-glycols, cyclic acetals are produced of the type



By heating together ammonium salts and aqueous formaldehyde, the ammonia undergoes methylation with the production of carbon dioxide and salts of monomethylamine and trimethylamine (Brochet and Cambier, Bull. Soc. chim. 1895, [iii], **13**, 533; Compt. rend. 1895, **120**, 557; Koeppen, Ber. 1905, **38**, 882). Primary and secondary aliphatic amines may also be methylated in a similar manner. Mixtures of formaldehyde, formic acid and amines react in accordance with the following equation:

$$R_2NH+CH_2O+H{\cdot}COOH = R_2N{\cdot}CH_3+CO_2+H_2O.$$

(Sommelet and Ferrand, Bull. Soc. chim. 1924, [iv], **35**, 446; Clarke, Gillespie and Weisshaus, J. Amer. Chem. Soc. 1933, **55**, 4571).

Analysis.—For the qualitative detection of formaldehyde, a large number of tests have been advanced, most of which are colour reactions. These include the formation of a red colour (changed to bluish-violet by addition of hydrochloric acid) with Schiff's reagent; reaction with phloroglucin in alcoholic alkali solution to give red colour; development of a yellow colour, later changing to red, in presence of resorcinol and sulphuric acid; as well as reaction with phenylhydrazine and sodium nitroprusside in alkaline solution. Most of the above reactions are suitable for detecting formaldehyde in dilutions of 1:50,000 (Sabalitschka and Harnisch, Z. anal. Chem. 1927, **70**, 67; *cf.* FOOD PRESERVATIVES, p. 297). Other tests for formaldehyde include the formation of a silver mirror from alkaline silver solutions, and the formation of characteristic derivatives such as anhydroformaldehydeaniline, hexamethylenetetramine and formaldehyde-*p*-nitrophenylhydrazone.

Of the numerous methods advanced for the quantitative determination of formaldehyde, that of Legler (Ber. 1883, **16**, 1335), based on the formation of hexamethylenetetramine, gives slightly low results. The accurate method of Blank and Finkenbeiner (*ibid.* 1898, **31**, 2979; 1899, **32**, 2141) depends upon the oxidation of formaldehyde by hydrogen peroxide in alkaline solution according to the equation,

$$2CH_2O+2NaOH+H_2O_2 =2H{\cdot}CO_2Na+H_2+2H_2O,$$

the excess alkali being determined by titration. In alkaline solution, formaldehyde is oxidised to formic acid by iodine, 2 atomic proportions of which are equivalent to 1 mol. of formaldehyde. This is the basis of Romijn's method (Z. anal. Chem. 1897, **36**, 18) which, however, fails in the presence of acetaldehyde. Another method, improved by Schulek (Ber. 1925, **58**, 732), depends on the combination of formaldehyde with potassium cyanide to form glycollonitrile, subsequently hydrolysed to potassium glycollate. This is said to be very satisfactory even in the presence of other aldehydes. For determining formaldehyde in dilute solutions, Orchard (Analyst, 1897, **22**, 4) has proposed a method based on the reaction with an ammoniacal silver solution, the excess silver being found volumetrically. Methods based on the combination of formaldehyde with sodium sulphite according to the equation,

$$CH_2O+Na_2SO_3+H_2O =CH_2O{\cdot}NaHSO_3+NaOH,$$

with titration of the alkali liberated, are not satisfactory in the presence of other aldehydes. For a review of the subject, *see* Mach and Herrmann, Z. anal. Chem. 1923, **63**, 417.

Uses of Formaldehyde.

Formaldehyde is employed extensively in industry and is to-day one of the most important organic chemicals of commerce. Very large quantities, amounting to thousands of tons per annum, are employed in the manufacture of synthetic resins and lacquers by condensation with phenols or urea. Condensation products of formaldehyde with various natural products, including casein, gelatin and yeast, with or without phenol or urea, are also employed extensively as resins. The most important synthetic resins are, however, those produced from formaldehyde and phenol, alkylphenols or urea.

On account of its intense chemical reactivity, this substance is used very extensively as an intermediate in the manufacture of dye-stuffs, such as indigo, rosaniline, auramine, acridine dyes, etc., for the production of pentaerythritol for explosives, and of numerous other chemicals. Substances such as paraformaldehyde, sodium formaldehyde bisulphite and sodium formaldehydesulphoxylate also find extensive application in dyeing, bleaching, calico printing, etc.

For the antiseptic properties of formaldehyde (*v.* Disinfectants, Vol. IV, 26*c*). Many pharmaceutical preparations containing formaldehyde, admixed or combined with other materials, have been placed on the market as medicines, general antiseptics, deodorants and internal antiseptics. Formaldehyde in 2–2·5% aqueous solution is employed in the disinfection of wool and hairs, and is said to be the most economical and efficient material for combating the anthrax bacillus. It is useful as a disinfectant in breweries, sugar refineries and stables, for combating parasites in both plants and animals, in agriculture and gardening for the partial sterilisation of soils, particularly for the intensive cultivation of tomatoes and cucumbers, and for many similar purposes. Its use in food preservation has been almost universally prohibited, but it is valuable in the preservation of anatomical and histological specimens and for fixing bacterial growths in gelatine.

On account of its ability to render gelatine and glue permanently insoluble, formaldehyde is used in the textile and paper industries for the waterproofing of fabrics and the fixing of glues and sizes, also in photography. An important application of formaldehyde in the textile industry is for increasing the fastness of dyes towards washing. Its hardening effect on proteins is utilised in the tanning of leather and treatment of silk. Viscose silk fibres were at one time hardened and thus strengthened by means of formaldehyde (Sthenosising).

H. M. S.

"FORMALIN." (*v.* Vol. IV, 26*c*).

FORMALS (*v.* Vol. I, 34*a*).

FORMAMIDE, $HCO{\cdot}NH_2$, is obtained by the action of ammonia or urea and/or heat on ammonium formate or by the action of ammonia on formic alkyl esters (B.P. 476942). It is also formed by the interaction of carbon monoxide and ammonia in ultra-violet light, in an electric discharge, or even in presence of an alkali alkoxide (U.S.P. 1787483). Laboratory preparations of formamide have been reviewed by Magill (Ind. Eng. Chem. 1934, **26**, 611).

Formamide is a hygroscopic liquid, m.p. +4°, b.p. 105–106°/10 mm. It may be dehydrated to hydrocyanic acid and readily hydrolysed by alkali into formates and ammonia. Replacement of the amido-hydrogen atoms may be effected to give simple metallic derivatives, but direct action of alkali metals affords derivatives of diformamide $(HCO)_2NH$ (Rakshit, J.C.S., 1913, **103**, 1557).

Formamide has been examined as a fertiliser (Rehling and Taylor, J. Amer. Soc. Agron. 1937, **29**, 134) and compares favourably with ammonium salts and urea (Brown and Reid, Soil Sci. 1937, **43**, 341).

FORMAMIDINE, $NH{:}CH{\cdot}NH_2$, is obtained from the hydrochloride of formimide or from dichloromethylformamidine by treating with absolute alcohol (Gautier, Ann. Chim. Phys. 1869, [iv], **17**, 133), or by the action of ammonia on formimino ethers. Only salts of formamidine are known, *e.g.* the hydrochloride, CH_4N_2,HCl, m.p. 81°, as the free base decomposes into its formates and ammonia when liberated from its salts. The salts themselves decompose on slight heating, *e.g.* formamidine hydrochloride yields hydrocyanic acid and ammonium chloride above 100°.

"FORMAMINE" (*v.* Vol. I, 326*a*).

"FORMAN." A name applied to chloromethyl menthyl ether, $C_{10}H_{19}{\cdot}O{\cdot}CH_2Cl$, formed by the action of formaldehyde on menthol in the presence of hydrogen chloride. A colourless fuming oil, b.p. 160–162°/16 mm. (Wedeland, Ber, 1901, **34**, 813). Employed in medicine in catarrhous affections of the air passages.

FORMANILIDE, $HCO{\cdot}NH{\cdot}C_6H_5$, m.p. 46°, is obtained by heating aniline with formic acid or esters thereof (Hartogs, Hollemann and van der Linden, Ber. 1911, **44**, 715), with oxalic acid, etc. The imino hydrogen atom is replaceable by sodium, mercury and other metals (Comstock, *ibid.* 1890, **23**, 2274). Halogenation with alkali hypohalogenite gives N-halogenoformanilides, but nuclear halogeno-, nitro- and other substitution products may be obtained by direct substitution. Formanilide is converted by hydrochloric acid at 100° into N:N′-diphenylformamidine, a compound used in the preparation of cyanine dyestuffs such as Astraphloxine.

FORMIC ACID, ($H{\cdot}COOH$), was discovered in 1760 by Rey, who obtained it by distilling red ants with water. It occurs in stinging nettles, in many fluids of animal origin such as sweat, urine and muscular plasma, and among the products of the bacterial oxidation of polyhydric alcohols and of carbohydrates. It is formed in the dry distillation of starch, sugar, gum, tartaric and oxalic acids, etc. It may be prepared by dissolving acetylene in fuming sulphuric acid, diluting with water, and boiling with baryta, the soluble barium formate remains in solution. It is best made in the laboratory by heating a mixture of crystallised oxalic acid with anhydrous glycerol (or other polyhydric alcohol of high boiling-point). The reaction begins at about 80° and carbon dioxide is evolved. The temperature is maintained at 105–110° until the gas evolution slackens, when a fresh quantity of oxalic acid is added and the process repeated.

The interpretation of the reaction usually accepted is as follows: The oxalic acid decomposes into water, carbon dioxide and formic acid which reacts with the glycerol, forming monoformin ($HCO{\cdot}OC_3H_5(OH)_2$); on addition of more crystallised oxalic acid, the water of crystallisation hydrolyses the monoformin to glycerol and formic acid, which distils over. Monoformin is thus continually formed and hydrolysed with the eventual production of formic acid of from 87–88% strength (Lorin, Bull. Soc. chim. 1866, [ii], **5**, 7; 1873, [ii], **20**, 241; 1875, [ii], **24**, 22, 436).

According to Chattaway (J.C.S., 1914, **105**, 151; 1915, **107**, 407), glyceryl oxalate and glyceryl acid oxalate are the first products of the reaction. The latter is unstable at a slightly higher temperature and decomposes, giving carbon dioxide and monoformin. The further addition of oxalic acid displaces formic acid from the monoformin.

Formic acid is now made industrially by direct synthesis from steam and carbon monoxide with the aid of a suitable catalyst. The types of catalyst which may be used are as follows:

(1) Free halogens or hydrogen halides with a carrier such as activated charcoal.
(2) Halides, especially iodides, of many bivalent metals.
(3) Non-volatile acidic oxides or the acid salts of these with the alkaline earth metals.

The reaction is usually carried out at temperatures of the order of 200–300°C., but the pressures employed vary within wide limits up to as much as 2,000 atm. For details of the process, *see* E. I. Du Pont de Nemours & Co., B.P. 406344, 406345; U.S.P. 1949825, 2001659, 2023003; Fawcett, Gibson and I.C.I., Ltd., B.P. 447492; Dreyfus, U.S.P. 2028764, 2028765; *see also* A. L. Andrikides, Dissertation, Leipzig, 1931.

Formic acid is also obtainable by the hydrogeneration of carbon dioxide in the presence of an amine and a catalyst. "Raney nickel," at 80°C., or sheet brass, at 250°C., may be used. Below 100°C. the reaction results in the amine salt, above this temperature the amide is formed. (Farlow and Adkins, J. Amer. Chem. Soc. 1935, **57**, 2222). Formic esters, which have recently become available by synthetic methods (*v. infra*), are a further potential source of the acid.

Until recently the formates (*v. infra*) were the starting point for the manufacture of formic acid. It may be obtained from these by treatment with mineral acids under suitable conditions. Thus, sulphuric acid may be used if the formic acid is continuously removed by entrainment in the vapour of some volatile hydrocarbon (Schering-Kahlbaum A.-G., G.P. 583764); *see also* Chem. Zentr. 1912, I, 1266; II, 163. Alternatively, formates may be treated *in vacuo* with acids or acid salts (Hempel, B.P. 3428, 1908) or distilled with nitric acid (R. Koepp & Co., Oestrich, Rheingau, G.P. 288266; Gewerkschaft Victor, G.P. 592054; 602999; 607379; Amer. Chem. Abstr. 1934, **28**, 2728; 1935, **29**, 818, 1835). By heating in a still 1 part of sodium formate with 2 parts of sodium hydrogen sulphate or other acid salt, acid from 97 to 98% is obtained (Chem. Fabr. Grünau Landshoff and Meyer A.-G., B.P. 14438, 1906). A concentrated acid is also obtained by treating alkali formates in solution in concentrated formic acid with dry hydrogen chloride, adding more formate to take up the excess of hydrochloric acid, and distilling (R. Koepp & Co., Chem. Fabr. A.-G., B.P. 414312).

Aqueous formic acid may be concentrated by distillation in the presence of a high boiling organic base which gives acid or neutral formates. Water first distils, followed by formic acid. The efficiency of the process is enhanced by adding also a hydrocarbon such as toluene or xylene to the mixture distilled (azeotropic distillation) (Lüscher and Lonza A.-G., G.P. 614860; R. Koepp, F.P. 778930; U.S.P. 2034332). An almost anhydrous acid is obtained by the following procedure. A mixture of technical, 85% formic acid (1 part) with phthalic anhydride (3 parts) is heated to the boiling-point and the exothermic reaction allowed to subside. It is heated for a further 2 hours, then allowed to stand overnight and the concentrated acid distilled off. Yields of 75–100% are obtained of an acid of freezing point 8·05°C.; d_4^{20} 1·2198 (Pryanishnikov and Shakhova, J. Gen. Chem. (U.S.S.R.), 1932, **2**, 821; Amer. Chem. Abs. 1933, **27**, 2672; *see also* B.P. 308731). A somewhat similar process has been described by Ritter (Ind. Eng. Chem. 1935, **27**, 1224).

Anhydrous formic acid is obtainable by the classical method of gently heating lead formate with sulphuretted hydrogen. It may also be prepared by heating the dehydrated sodium salt with anhydrous oxalic acid, by distilling the ordinary acid at reduced pressure over anhydrous copper sulphate (Parker, J. Amer. Chem. Soc. 1911, **46**, 236) or phosphoric oxide (Jones, J.S.C.I. 1919, **38**, 362T), or by the method of fractional freezing (Ewins, J.C.S. 1914, **105**, 352). It is a colourless, slightly fuming liquid with a penetrating odour, and is intensely corrosive. It has b.p. (corrected) 100·5°; 50°/120 mm.; m.p. 8·4°; $d_4^{15}=1{\cdot}226$, $d_4^{20}=1{\cdot}220$; $n_D^{20}=1{\cdot}3714$; $k=2{\cdot}4\times10^{-4}$ at 25°. The vapour pressure of the pure acid is at 10°, 19·88 mm., and at 20°, 33·54 mm. (Collidge, J. Amer. Chem. Soc. 1928, **50**, 2166). The heat of combustion, C_p (liq.) is 61·7 kg.-cal.; C_p (vap.), 69·4 kg.-cal. It is miscible in all proportions with water, alcohol and ether. The specific gravity of its aqueous solution is given in the following table (Richardson and Allaire, Amer. Chem. J. 1897, **19**, 150).

%	d_4^{20}	%	d_4^{20}.
10	1·0247	60	1·1425
20	1·0489	70	1·1656
30	1·0730	80	1·1861
40	1·0964	90	1·2045
50	1·1208		

The vapour of formic acid burns with a blue flame.

Formic acid is readily decomposed catalytically according to one or more of the following equations:

$$\text{(1)}\quad H{\cdot}COOH=CO_2+H_2;$$
$$\text{(2)}\quad H{\cdot}COOH=CO+H_2O;$$
$$\text{(3)}\quad 2H{\cdot}COOH=H{\cdot}CHO+CO_2+H_2O.$$

By leading the vapour over the following heated substances it is decomposed in accordance with equation (1) at varying rates: palladium, platinum, copper, nickel, cadmium and oxides of zinc and tin. Palladium sponge and platinum sponge bring about total decomposition at 245° and 215° respectively. Titanium dioxide and the blue oxide of tungsten favour decomposition according to equation (2). Powdered pumice, magnesia and wood charcoal behave similarly. With silica, zirconia, alumina and uranium dioxide some formaldehyde is formed in addition to carbon monoxide and water, and with thoria all three reactions are possible (Sabatier and Mailhe, Compt. rend. 1911, **152**, 1212). By passing the vapour of formic acid over alumina at 287° a gas containing 92% of carbon monoxide may be obtained (Westcott and Engelder, J. Physical Chem. 1926, **30**, 476). More recently Graeber and Cryder (Ind. Eng. Chem. 1935, **27**, 828), in a comprehensive study of the catalytic production of carbon monoxide from formic acid, obtained 95% yields of the gas using a thoria upon silica-gel catalyst at 300°C. The same reaction is said to be catalysed by selenic acid (Dolique, Bull. Soc. chim. 1935, [v], **2**, 1489). Carbon monoxide is also obtained when formic acid is treated with cold concentrated sulphuric acid. If excess of formic acid is employed, evolution of the gas proceeds indefinitely, but at a constantly decreasing rate owing to the diluent action of the water formed in the reaction (Schierz and Ward, J. Amer. Chem. Soc. 1928, **50**, 3240; DeRight, *ibid.* 1933, **55**, 4761).

The photochemical decomposition of the acid has been studied by Gorin and Taylor (*ibid.* 1934, **56**, 2042).

Detection and Estimation.—Formic acid may be detected by the following reactions. With concentrated sulphuric acid, formic acid and the formates evolve carbon monoxide in the cold. With ferric chloride, neutral formate solutions give a red colour and on boiling a brown precipitate of basic ferric formate is thrown down. Formic acid and formate solutions reduce silver nitrate to silver. Similarly mercuric chloride is reduced to mercurous chloride, and, if excess of formic acid or formate be present, to metallic mercury. If a solution containing the free acid is digested with magnesium, formaldehyde is produced (Fincke, Biochem. Z. 1913, **51**, 258). When formic acid is warmed with aqueous sodium bisulphite a green to blue colour is developed adding sodium nitroprusside (Comanducci, Chem. Zentr. 1919, II, 226). For identification in the presence of hydrochloric acid by heating with chromic acid mixture, *see* Sulzer Z. angew. Chem. 1912, **25**, 1273.

Formic acid may be estimated by the method of Jones (J. Amer. Chem. Soc. 1895, **17**, 539). The solution is made alkaline with sodium carbonate, warmed, and an excess of standard permanganate added. The solution is acidified and a measured volume of standard oxalic acid solution is run in, until the precipitate of manganese hydroxide has dissolved and the permanganate disappeared. The excess of oxalic acid is back titrated with permanganate (*see also* Rupp, Z. anal. Chem. 1906, **45**, 687; Grossmann and Aufrecht, Ber. 1906, **39**, 2455). Other methods depend upon the reduction of mercuric to mercurous chloride (Riesser, Z. physiol. Chem. 1915, **96**, 355; Biochem. Z. 1923, **142**, 280), the titration of the acid with standard alkali or the decomposition of the acid in the carbonic acid apparatus with oxidising agents (Rupp, Arch. Pharm. 1905, **243**, 69; Wiehe and Jacobs, Ind. Eng. Chem. [Anal.], 1936, **8**, 44). It may be estimated in the presence of acetic acid by the method of Stainier and Massart (Amer. Chem. Abs. 1936, **30**, 5906). The acids are heated with potassium iodate solution and after neutralisation with calcium carbonate the liberated iodine is titrated with standard thiosulphate solution. For its estimation in the presence of lactic acid, *see* Jamet (*ibid.* 1935, **29**, 7870), and of various other substances, *see* Fincke (Biochem. Z. 1913, **50**, 253; Analyst, 1913, **38**, 378).

Formic acid is a strong reducing agent, a powerful antiseptic and has been used as a food preservative (Woodman and Burrell, Tech. Quart. 1908, **21**, 1; this vol. p. 305). For its use as a solvent for organic and inorganic substances, *see* Aschan (Chem.-Ztg. 1913, **37**, 1117). It is used in dyeing as an assistant or reducing agent with potassium dichromate mordant and also in dyeing woollen goods or unions with acid dyestuffs (Kapff, J.S.C.I. 1905, **24**, 129; Mettner, *ibid.* 434; and Rusby, *ibid.* 1907, **26**, 467).

Salts.—Industrial methods for the preparation of the formates are based upon three reactions: (1) The interaction of carbon monoxide and metallic oxides. In this method carbon monoxide under pressure is passed over metallic oxides, basic minerals or alkali hydroxides, or into aqueous suspensions of alkaline earth hydroxides. The conditions vary slightly in the different processes; alkali formates, potassium ferrocyanide and the chlorides of palladium and platinum have been used as promoters (B.P. 4471, 1908; 13953, 1907; F.P. 382001, 389065; U.S.P. 875055; G.P. 179515; J.S.C.I. 1908, **27**, 420, 769, 898; Koepp & Co., G.P. 209417, 590635, 602744; B.P. 415871; Chem. Zentr. 1909, I, 1785; Amer. Chem. Abstr. 1934, **28**, 3081; 1935, **29**, 818; I.G. Farbenind. A.-G., B.P. 413240; F.P. 794100; Amer. Chem. Abstr. 1936, **30**, 4514; Chem. Fabr. Kalk. G.m.b.H. and Oehme, G.P. 622149; Amer. Chem. Abstr. 1936, **30**, 1393). (2) The hydrolysis of the cyanides of the alkaline earth metals. These, on treatment with water vapour under pressure at temperatures below 300°, yield ammonia and a formate (Badische Anilin- u. Soda-Fabrik, F.P. 372714; J.S.C.I. 1907, **26**, 967). The interaction of a solution of potassium ferrocyanide with caustic potash according to the following equation has also been patented (Haakh, G.P. 281044).

$$K_4Fe(CN)_6+14H_2O= \\ 4HCO_2K+2HCO_2NH_4+4NH_3+Fe(OH)_2$$

(3) The reduction of carbonic acid or its salts with hydrogen. Rogatien (B.P. 12604, 1893; J.S.C.I. 1893, **12**, 864) obtained ammonium formate and bicarbonate by passing moist nitrogen, hydrogen and carbon dioxide over slightly heated pumice or other absorbent bodies. A 100% yield of calcium formate may be obtained from calcium carbonate if the latter is heated with hydrogen under 50 atm. pressure and carbon dioxide (20 atm.) at 70° in the presence of spongy palladium for 4½ hours (Bredig and Carter, Ber. 1914, **47**, 541). The bicarbonates of the alkali metals and of ammonia may be reduced in aqueous solution with hydrogen under pressure in the presence of a suitable catalyst, such as palladium black (B.P. 801, 1915; 9762, 1915), nickel upon coke (Leroux, U.S.P. 1995211).

Decomposition of the Formates.—The formates of the alkali metals when heated alone in absence of air to 400° decompose, giving mainly hydrogen and oxalic acid; at lower temperatures carbonates are chiefly formed. Alkaline earth formates give only carbonates. Under certain conditions some formaldehyde may be formed in the reaction (Hofmann and Schumpelt, Ber. 1916, **49**, 303). The pyrolysis of mixtures of sodium formate and sodium hydroxide has been studied by Balandin and Freĭdlin (J. Gen. Chem. Russ. 1936, **6**, 868). With mixtures containing one equivalent or more of hydroxide to one of formate, the reaction begins at 210°C. and proceeds smoothly at 250°C.; hydrogen is evolved and sodium carbonate produced. With mixtures containing alkali in lower ratio, sodium oxalate is formed, but not below 270°C. Industrial methods for the production of oxalates from formates depend upon the latter reaction (Koepp & Co., F.P. 759253; Enderli and Schrodt, U.S.P. 2033097; Amer. Chem. Abstr. 1936, **30**, 2580).

Potassium formate, (HCO_2K), and *sodium formate*, (HCO_2Na), are readily soluble deliquescent salts which, according to Bineau, form acid salts on solution in hot concentrated formic acid. *Calcium formate*, $(HCO_2)_2Ca$, and *barium formate*, $(HCO_2)_2Ba$, crystallise in rhombic prisms, readily soluble in water, insoluble in alcohol. *Lead formate*, $(HCO_2)_2Pb$, is less soluble in water than other formates, 1 part dissolving in 63 parts of water at 16°, and is insoluble in alcohol; on warming the solution with lead oxide there is formed a series of basic formates, which have an alkaline reaction and crystallise in needles. *Copper formate*,

$$(HCO_2)_2Cu,4H_2O,$$

crystallises in light blue monoclinic prisms and forms basic salts (J.C.S. 1915, **107**, 1281). *Silver* and *mercurous formates* decompose even in the dark; the latter deflagrates when heated and decomposes on percussion. *Chromous formate*, $Cr(HCO_2)_2,2H_2O$, forms red cubes (Traube and Goodson, Ber. 1916, **49**, 1679).

Formic esters.—These are now obtained, in a manner analogous to that used for the direct synthesis of formic acid and the formates, by the interaction of anhydrous alcohols with carbon monoxide under pressure. Thus when methyl alcohol containing sodium methoxide is heated to 60–65°C. with carbon monoxide under 50 atm. pressure for 2 hours and the temperature then allowed to fall, methyl formate is obtained in circ. 60% yield (Ges. für Kohlentechnik, G.P. 588763; 591581; 595307; Amer. Chem. Abstr. 1934, **28**, 2014; *also* Chr. Ammon, F.P. 776616; Amer. Chem. Abstr. 1935, **29**, 3690). A recent method of preparation of the formic esters of some higher aliphatic alcohols consists in treating the lighter fractions obtained in the "cracking" of petroleum oils with formic acid containing a little sulphuric acid. Slow addition of formic acid to the olefins occurs, with the eventual production of secondary and tertiary amyl and hexyl formates (Sucharda and Mazonski, Przemysł Chem. 1933, **17**, 41; Amer. Chem. Abstr. 1933, **27**, 5954).

Methyl formate boils at 30·4°/712 mm.; sp.gr. 0·9928. It can be made by the method described above or by passing the vapour of methyl alcohol over a dehydrogenating catalyst such as copper at 150–250° (Compagnie de Béthune, F.P. 673337). It can also be prepared by acting on dry sodium formate with a mixture of methyl alcohol and aqueous hydrochloric acid, or by digesting methyl alcohol with concentrated formic acid.

Ethyl formate, b.p. 50·4°, sp.gr. 0·9445, can be made by heating a mixture of 6 parts of alcohol (90%), 7 parts of sodium formate and 10 parts of concentrated sulphuric acid. Other esters have the properties given below. *Propyl*, b.p. 81°, d_4^{20} 0·9058; *allyl*, b.p. 83°, d_0^{17} 0·932; n-*amyl*, b.p. 130°, d_4^0 0·9018; *benzyl*, b.p. 203°/747 mm.; d_4^{23} 1·081. p-*bromphenacyl* (Hurd and Christ, J. Amer. Chem. Soc. 1935, **57**, 2007), m.p. 140°.

"FORMICIN." Hydroxymethylacetamide, $\mathrm{CH_3{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}OH}$.

"FORMIDIN." Methylene disalicylic iodide, $\mathrm{C_{15}H_{10}O_2I_6}$.

"FORMIN" (*v.* Vol. I, 326*a*).

FORMINS. The term formin is given to an ester formed by the condensation of a polyhydric alcohol with formic acid although its use is commonly restricted to derivatives of trihydroxy alcohols.

I. Formins of Dihydroxy Alcohols.

(*a*) **Ethylene Glycol Monoformin,** $\mathrm{HO{\cdot}CH_2{\cdot}CH_2O{\cdot}OCH}$, prepared from ethylene glycol and 95% formic acid (M. H. Palomaa, Chem. Zentr. 1913, II, 1956). It is obtained when ethylene diformin is boiled with an excess of anhydrous ethyl alcohol for 8 hours (Henry and Dewael, Chem. Zentr. 1902, II, 928). It may also be obtained together with ethylene diformin by boiling ethylene glycol with 75–80% formic acid (Henninger, Ber. 1874, **7**, 263). The *monoformin* which hydrolyses in water, has been formed in anhydrous medium by using formamide acid sulphate,

$$\mathrm{ROH+HCONH_2,H_2SO_4}$$
$$\mathrm{=HCOOR+(NH_4)HSO_4}$$

(P. Magill, Ind. Eng. Chem. 1934, **26**, 611). It is a liquid: b.p. 179–180·5°/766 mm., d_4^{15} 1·1989 (Palomaa, *l.c.*). Its velocity of esterification in formic acid under certain conditions has been determined (A. Kailan and G. Brunner, Monatsh. 1929, **51**, 334).

(*b*) **Ethylene Glycol diformin,**

$$\mathrm{HCO{\cdot}OCH_2{\cdot}CH_2O{\cdot}OCH},$$

is prepared by boiling ethylene glycol with 75–80% formic acid and treating the mixture of mono- and di-formins, so obtained, with anhydrous formic acid (Henninger, Ber. 1874, **7**, 263). It is also produced from ethylene glycol and an excess of formic acetic anhydride (a molecular mixture of acetic anhydride and formic acid) (Béhal, Ann. Chim. Phys. 1900, [vii], **20**, 424). It has been obtained together with other products from oxalic acid and ethylene glycol (Lorin, Bull. Soc. chim. 1874, [ii], **22**, 104). It is a liquid, b.p. 174° (Henninger, *l.c.*), 88–89°/25 mm., d^0 1·193 (Béhal, *l.c.*).

(*c*) **Pinacone Monoformin,**

$$\mathrm{HCO{\cdot}OCMe_2{\cdot}CMe_2{\cdot}OH},$$

is prepared from formic acetic anhydride and pinacone (Béhal, *l.c.*, b.p. about 90°/20 mm.).

II. Formins of Trihydroxy Alcohols.

A. Glycerol Formins.

In general the esterification of glycerol with formic acid gives mainly diformins and the acid appears to act more easily on the secondary alcoholic group since 1:2-di- and 2-monoformins are the esters which predominate.

(*a*) *Glycerol Monoformins,* $\mathrm{HCO{\cdot}OC_3H_5(OH)_2}$. A mixture of the monoformins is produced in the preparation of formic acid by heating glycerol with oxalic acid at 190° (Tollens and Henninger, Bull. Soc. chim. 1869, [ii], **11**, 395, and is extracted from the mixed product by means of ether.

(i) **α-Glyceryl formate** synthesised from α-chlorohydrin and sodium formate contains 87% ester, and is unstable, decomposing at 150° *in vacuo*, or suddenly below 220° yielding only 4% allyl alcohol (Delaby and Dubois, Bull. Soc. chim. 1930, [iv], **47**, 565).

(ii) **β-Glyceryl formate.**—A monoformin is obtained as intermediate in the formic acid method for the preparation of allyl alcohol (Organic Syntheses, 1921, **1**, 15, and 1926, **6**, 103). It has the following properties: b.p. 154–7°/10 mm.; d_0^0 1·3052; $n_D^{12\cdot5}$ 1·4614; 1 gm. mol. of β-formate decomposes smoothly at 235° to yield oxides of carbon 22·4 l., $\mathrm{H_2}$, and saturated hydrocarbons, and 57% allyl alcohol partly as allyl formate. Since the α-ester produces only 4% allyl alcohol, it is assumed that this esterification product must consist mainly of the β-ester (R. Delaby and P. Dubois, Compt. rend. 1928, **187**, 949).

(*b*) *Glycerol Diformins* $\mathrm{(HCO{\cdot}O)_2C_3H_5{\cdot}OH}$. A diformin is obtained by heating oxalic acid with glycerol at 140°, extracting with ether and distilling under reduced pressure, b.p. 163–166°/20·30 mm.; d^{15} 1·304 (van Romburgh, (Compt. rend. 1881, **93**, 847). It is insoluble in carbon disulphide and decomposed by water with the formation of glycerol and formic acid.

In the formic acid method for the preparation of allyl alcohol (Organic Syntheses, 1921, **1**, 15; 1926, **6**, 103) a diformin may be isolated as intermediate product, $b{\cdot}p_{15}$ 148–9° 15 mm., d_0^0 1·3209, $n_D^{23\cdot4}$ 1·4492 (Dalaby and Dulong, Compt. rend. 1928, **187**, 768.

Glyceryl diformate, b.p. 158–160°/18 mm., may be obtained in very good yield from glycerol, 80% formic acid and toluene—an azeotropic mixture (M. A. Wahl, Bull. Soc. chim. 1925, [iv], **37**, 713).

These diformates obtained by esterification probably contain a preponderance of the αβ-ester (R. Delaby and P. Dubois, Compt. rend. 1928, **187**, 949).

(i) **αγ-Glyceryl diformate** has been synthesised from 1:3-dichlorohydrin, b.p. 144–6°/11 mm.; d_0^0 1·3218; $n_D^{18\cdot3}$ 1·4486. It is very hygroscopic, soluble in alcohol, acetone, slightly soluble in ether, insoluble in benzene (Delaby and Dubois, Compt. rend. 1928, **187**, 767).

(ii) **αβ-Glyceryl diformate** has also been synthesised from 1:2-dibromohydrin, b.p. 151–3°/17 mm., d_0^0 1·3252, d_0^{17} 1·3214, n_D^{17} 1·4503. It has similar solubility characteristics to the αγ-compound (Delaby and Dubois, *ibid.*).

The αγ- and αβ-diformates yield 44·8 l. oxides of carbon and 43 and 46 g. per gm. mol. respectively of allyl alcohol at 255–310°. The velocity of esterification has been determined (A. Kailan and C. Brunner, Monatsh. 1929, **51**, 334).

(*c*) **Glycerol triformin,** $\mathrm{(HCO{\cdot}O)_3C_3H_5}$, is prepared by repeatedly heating glycerol with 100% formic acid, the excess acid being distilled off each time until a rich triformin mixture is obtained. The viscous product is cooled in liquid ammonia when the triformin crystallises out. Pure triformin is colourless; m.p. 18°, b.p. 266°/762 mm.; $n_D^{18°}=1·4412$. It is hydrolysed slowly by cold, readily by hot water (van Romburgh, Z. physikal, Chem. 1910, **70**, 459).

B. αγ-Dimethylglycerol Formins.

(*a*) A mixture of *mono- and di-formins* may be prepared by refluxing dimethylglycerol for 6 hours at 150–170° with excess 96% formic acid and distilling the product in vacuum, the fraction b.p. 151·3–153·5°/19 mm. consists mainly of the diformate. When the mixture is heated to 200° decomposition ensues leaving the *triformin.*

(*b*) **αγ-Dimethylglycerol triformin** has m.p. 85°, b.p. 130–134°/15 mm. (Delaby and Morel, Bull. Soc. chim. 1926, [iv], **39**, 416).

C. α-Methyl γ-Ethyl Glycerol Formins.

(*a*) *A Mixture of Formins* has been isolated by heating methylethylglycerol with formic acid. On heating the product to 200° ethyl propylene carbinol is obtained together with a non-volatile residue of the *triformin*, m.p. 94·5° (Delaby and Morel, *l.c.*).

D. Ethylglycerol Formins.

(*a*) *Mono- and Di-Formins* are formed mixed with unchanged ethylglycerol when ethylglycerol is boiled with 2·5 times its weight of crystalline formic acid for 6 hours and distilled, the fraction b.p. 150–2°/15 mm. corresponds to a diformin. At 270° it gives water, formic acid and α-ethylvinyl-carbinol (b.p. 114–116°) and Δ^{β}-penten-α-ol (b.p. 139–140°, d_4^0 0·864, d_4^{15} 0·855, n_D^{15} 1·4378).

(*b*) The residue from the above distillation solidifies at 60–61° and is the *triformin* derivative (Delaby, Compt. rend. 1923, **176**, 1898).

III. Miscellaneous Formins.

(*a*) **Erythritol Tetraformin,**

$$C_4H_8(O·OCH)_4,$$

prepared by boiling 1 part of erythritol first with 18 parts of formic acid of sp. gr. 1·18 and then with 10 parts of crystalline formic acid. Distilling off the excess acid, heating the residue to 200° and extracting with absolute alcohol. The solvent is evaporated off and the residue recrystallised from alcohol in colourless needles, m.p. 150° (Henninger, Compt. rend. 1884, **98**, 149).

(*b*) **Dipentaerythritol Hexaformin,**

$$O[CH_2·C(CH_2O·OCH)_3]_2,$$

prepared by refluxing dipentaerythritol in conc. formic acid and fuming off twice with formic acid at 120°. It is a yellow solid, m.p. 56° (W. Friederich and W. Brün, Ber. 1930, **63** [B], 2681).

(*c*) **Cellulose Formins** are readily obtained by heating cellulose with anhydrous formic acid in presence of a catalyst (*e.g.* $ZnCl_2$). The solvents which dissolve these esters, such as pyridine and formic acid, are however highly inconvenient in the manufacture of films and fibres (B. 1931, 1087). For further information, *see* H. Mark, "Physik und Chemie der Cellulose," J. Sprenger, Berlin, 1932; J. T. Marsh and F. C. Wood, "Chemistry of Cellulose," Chapman and Hall, London, 1938.

"FORMOL" (*v.* Vol. IV, 26*c*).

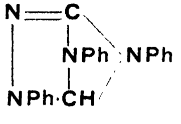
FORMOLITES. A term applied sometimes to all formaldehyde resins but preferably restricted to those resins derived from hydrocarbons, *e.g.* in presence of sulphuric acid. Unsaturated and aromatic hydrocarbons react in this way and products obtained by reaction of such constituents of lubricating and other oils serve both to refine the oils and provide plastics which may be moulded (B.P. 289920; G.P. 509305). The nature of the formolite varies from that of a sticky oil in the case of cracked gasolines (Ormandy and Craven, J. Inst. Petroleum Tech., 1924, **10**, 99) to coloured solid resins insoluble in water such as those from naphthalene and anthracene (Serverin, Mon. du petrole Roum. 1911, **21**, 22) and is strongly influenced by other factors such as the use of trioxymethylene in place of formalin. The formolite reaction has been used in the quantitative determination of reactive hydrocarbons in crude oils Nastukoff, J.C.S. 1904, **86**, i, 242, 801; Petroleum, 1909, **4**, 1336, 1911, **7**, 239; J. Russ. Phys. Chem. Soc. 1915, **47**, 46; J. Ind. Chem. Russ. 1925, **1**, 23; *cf.* Hošek, Chem. Obzor. 1929, **4**, 67) and according to recent investigations (Nastukoff, Petroleum, 1926, **22**, 1349; 1927, **23**, 1451) the determination of the so-called formolite number may be modified to afford a measure of asphaltic, light lubricating and other fractions of the oil in addition to an estimate of the total reactive hydrocarbons.

FORMOMONETIN *v.* *iso*Flavone (this Vol., p. 259*c*).

FORMOSANINE. The alkaloid of *Ouroupariaformosana* Mats. (Raymond-Hamet, Compt. rend. 1936, **203**, 1383).

"FORMOSUL," "FORMOSUL G." (*v.* Vol. IV, 148*c*, 149*c*).

"FORNITRAL" is the name given to the diformate of *nitron* (1:4-diphenyl-3:5-*endo*-anilodihydrotriazole)—



usually obtained in the form of flat needle crystals, m.p. 128°. Solubility in water 17%, and the solution is stable whilst that of nitron deteriorates. It may be used for the detection and estimation of nitric acid although it has not replaced nitron for this purpose. Of the more insoluble salts of fornitral may be mentioned: perchlorate (sol. 1:50,000), nitrate (1:60,000 at 15° and 1:80,000 at 0°), while the picrate is even less soluble.

1 c.c. of water containing 0·0075 mg., HNO_3, gives a ppt. after 5 hours with 5–6 drops of a 10% solution of fornitral (Ann. Chim. Analyt. 1921, [ii], **3**, 207; Analyst, 1921, **46**, 385).

"FORTOIN." A synonym for *Methylene-dicotoin*

$$CH_2(C_{14}H_{11}O_4)_2,$$

formed by the action of formaldehyde on cotoin. Used in the treatment of diarrhœa.

FORSTERITE. Mineral form of magnesium orthosilicate, Mg_2SiO_4.

"FOUADIN" (*v.* Vol. I, 439*a*).

FOULING OF SHIPS' HULLS (*v.* Vol. III, 383*b*).

"FOURNEAU 189" (*v.* Vol. I, 489*b*).

"FOURNEAU 270, 417" (*v.* Vol. I, 489*d*).

FOWLER'S SOLUTION, syn. Liquor Arsenicalis, B.P. A solution of potassium salts of arsenious acid used in medicine. It is conveniently prepared by neutralising with hydrochloric acid a solution of potassium meta-arsenite in water (Rosenthaler, Scientia Pharm. 1935, **6**, 41). Official preparation B.P. 1932, 162. Morton (Quart. J. Pharm. 1933, **6**, 1) concludes from conductivity measurements that the solution is one of arsenious oxide in potassium meta-arsenite.

FOXBERRY. The fruit of *Vaccinium vitis-idæa.* It is also known as the mountain cranberry or cowberry, and grows wild in central Europe, northern U.S.A. and Canada. The fruit resembles the common cranberry but is smaller.

Ystgaard (Tids. Norske Landw. 1902, **9**, 125) records the analysis of the whole fruit as:

Solids.	Protein.	Total acid.	Citric acid.
15·48	0·25	1·92	0·64

Malic acid.	Sugars.	Pentosans.	Fibre.
0·31	6·4	0·59	1·88

Hotter (Z. landw. Versuchsw. 1906, **9**, 747) quotes figures of a similar order and also reports the sugars as glucose 3·0–4·6, fructose 4·0–5·8, sucrose 0·4–0·8.

Analysis of foxberry juice by Windisch and Schmidt (Z. Unters. Nahr.-Genussm. 1909, **17**, 584) shows total solids 11·28, protein 0·12, acids (as citric) 1·92, invert sugar 6·47, sucrose 0·48, tannin 0·19, ash 0·32%.

The composition of the seeds of the foxberry is—

Water. %	Protein. %	Fat. %	*N*-free extract + fibre. %	Ash. %
5·97	23·2	30·12	38·56	2·11

The seeds yield a drying oil having the following characteristics: d_{15} 0·9301, n_{25} 1·4753, saponification value 190·1, iodine value 169·2, Reichert-Meissl value 0·55, Polenske value 0·30, acid value 1·94, Hehner value 95·7, bromides (linolic and linolenic acids) 22·8% (Diedrichs, Z. Unters. Nahr.-Genussm. 1912, **24**, 575).

In addition to citric and malic acids the berries contain small proportions of glyoxylic, *iso*valeric and benzoic acids. The presence of a glucoside, vacciniin, $C_6H_{11}(C_6H_5CO)O_6$, is also recorded by Griebel (*ibid.* 1910, **19**, 241).

A. G. Po.

FRAGARIANIN. A tannin contained in strawberry root, it yields on hydrolysis glucose and *fragarin* (Phipson, Chem. News, 1878, **38**, 135).

FRAGAROL. This name is to-day given to β-naphthyl *iso*butyl ether which has an odour somewhat resembling strawberries (genus *Fragaria*). It is a crystalline body melting at 32–34°, and is used in traces in some types of Eau de Cologne and Neroli perfumes. The name was originally applied to the ethyl ether, which is now known as *Bromelia.* Both the ethyl and the methyl ethers of β-naphthol are known as "*Nerolin,*" the former as Nerolin Bromelia, and the latter as Nerolin Yara Yara.

E. J. P.

FRANCKEITE. A complex sulphide ore of tin, $Pb_5FeSn_3Sb_2S_{14}$, containing, according to this formula, Sn 16·71%. It consists of platy, tetragonal crystals, with a perfect cleavage parallel to the surface of the folia, which are often aggregated in more or less pronounced radiating groups, sometimes forming spherules and reniform masses. It is iron-black with a bright metallic lustre; marks paper and is malleable, like graphite. The mineral occurs in some quantity near Chocaya and in the Trinacria mine at Poopó in Bolivia, and is known locally as *llicteria.* The above formula written in the form $3PbSnS_2+Pb_2FeSb_2S_8$ brings out a relation between franckeite and the allied Bolivian minerals *teallite* ($PbSnS_2$) and *cylindrite* ($3PbSnS_2+SnFeSb_2S_8$). Analyses I and II by G. T. Prior, 1904 (II on less distinctly crystalline material with some massive), III by C. Winkler, 1893 (also germanium about 0·1%, and gangue 0·71%):

	I.	II.	III.
Pb	46·23	48·02	50·57
Fe	2·69	2·74	2·48
Zn	0·57	—	1·22
Ag	0·97	0·99	n.d.
Sn	17·05	13·89	12·34
Sb	11·56	13·06	10·51
S	21·12	20·82	21·04
	100·19	99·52	98·97
Sp.gr. . . .	5·88	5·92	5·55

L. J. S.

FRANCOLITE (*v.* Vol. I, 449*d*).

FRANGULA consists of the bark of *Rhamnus frangula* Linn. (Fam. Rhamnaceæ), it contains the crystalline glycoside *frangulin* which yields on hydrolysis rhamnose and *frangulo-emodin* (1:6:8-trihydroxy-3-methylanthraquinone). Used as a mild purgative.

FRANGULIN *v.* FRANGULA.

FRANKINCENSE, *olibanum.* The gum-resin is the dried exudated juice of several species of *Boswellia.*

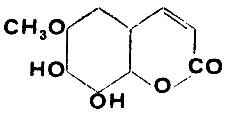
FRANKLINITE. A member of the spinel group of minerals with the general formula $R''O{\cdot}R_2'''O_3$, where R''=Fe, Zn, Mn, and R'''=Fe, Mn. The actual composition is very variable; ferric oxide always predominates (56–67%), zinc oxide ranges from 6 to 23%, and manganese oxides (MnO, Mn_2O_3) average 15–20%. The mineral occurs as well-developed crystals of octahedral habit, as rounded grains, and as granular masses. It is black with a sub-metallic lustre, much resembling magnetite in appearance, but is readily distinguishable from this in being only slightly magnetic. Sp.gr. 5·0–5·2; hardness, 6.

Although known only from Franklin Furnace in New Jersey (hence the name), it is found there in considerable abundance in association with ores of zinc in crystalline limestone. After the extraction of the zinc, the residue is used in the manufacture of spiegeleisen.

L. J. S.

" ***FRANKONIT*** *"* *v.* Earths, Active (Vol. IV, 248*c*).

FRAXETIN,



7:8-dihydroxy-6-methoxycoumarin, m.p. 227–228° (Wessely and co-workers, Ber. 1929, **62** [B], 120; Monatsh. 1932, **60**, 159) is the aglucone of fraxin.

FRAXIN *v.* Coumarin Glycosides (Vol. III, 413*a*).

FRAXINELLONE (*v.* Vol. III, 602*c*).

FRAXITANNIC ACID. A tannin found in the leaves of *Fraxinus excelsior* Linn.

FREESTONE. An indefinite term used by quarrymen for a rock which admits of being freely worked in any direction for use as a building stone. Such a rock shows a uniformity or evenness of grain and no distinct bedding. Many stratified rocks may be readily sawn when freshly quarried, and while holding the "quarry water," but acquire considerable hardness on exposure to the atmosphere. Most freestones are either limestones or sandstones. In the Inferior Oolite there are certain beds known to geologists as the Lower and Upper Freestones, which are largely quarried as building stones, near Cheltenham. The Bath stone from the Great Oolite, and the Portland stone from the Upper Oolites, are also well-known oolitic freestones. The term freestone is also applied to many of the red Permian and Triassic sandstones of the north-west of England, *e.g.* the St. Bees sandstone. Many of the Coal-measure sandstones admit of being readily cut and tooled, and, being without any marked tendency to split in definite directions, are valuable freestones; such, for instance, are the sandstones of Craigleith, near Edinburgh, and of Darley Dale in Derbyshire.

L. J. S.

FREEZING OR COOLING MIXTURES. The temperature of a substance may be reduced by bringing it in contact with other substances at a lower temperature. Such cooling is produced by freezing mixtures of which the most commonly used are cryohydrates. The list shown in the next column is of useful cryohydric mixtures made from readily available substances.

Temperatures down to −160°C. may be obtained by passing liquid nitrogen into pentane contained in a Dewar vessel. Light petroleum, b.p. 46°, is somewhat less satisfactory than pure pentane for this purpose.

A mixture of 2 parts ether and 1 part alcohol may be similarly cooled to temperatures down to −120° without solidification, or liquid air may be poured directly into such a mixture provided great care is taken to *remove all flames from the proximity.*

I. Aqueous Solutions.

	Grams anhydrous salt in 100 g. of water.	Cryohydric Temp. °C.
$Pb(NO_3)_2$ . .	35·2	−2·7
$MgSO_4,12H_2O$.	23·5	−3·9
$BaCl_2$ . . .	29	−7·8
$MnSO_4,7H_2O$.	47·5	−10·5
NH_4Cl . . .	22·9	−15·8
NH_4NO_3 . . .	70	−17·3
NaCl	28·9	−21·2
$MgCl_2,12H_2O$.	26	−33·6
$CaCl_2,6H_2O$.	42·5	−55
$ZnCl_2,4H_2O$ . .	104	*c.* −62

II. Mixtures with Solid Carbon Dioxide.

Substance.	Lowest temp. attainable. °C.
Ethylene dichloride . .	−60
Absolute alcohol. . . .	—72
Chloroform	—77
Ethyl ether	−77
Amyl acetate	−78
Methyl chloride	−82

Liquid air or liquid oxygen may be poured into a copper test tube suspended in the refrigeration bath, but on no account should liquid air or liquid oxygen come in direct contact with pentane (or the equivalent petroleum fraction). Should liquid air be used for cooling other highly inflammable substances such as CS_2, the use of the copper test tube referred to above is *essential* if explosion risk is to be eliminated.

FREIBERGITE (*v.* Vol. IV, 590*c*).

FREMONTITE (*v.* Vol. I, 303*d*).

' FRENCH CHALK ' (*v.* Vol. I, 162*c*).

FRENCH POLISH. A solution of shellac in alcohol; occasionally containing gum elemi and copal.

" ***FRENCH POUDRE B.*** *"* (*v.* Vol. IV, 518*b*).

" ***FRESOL*** *"* *v.* Creosote (Vol. III, 420*a*).

FREUND'S ACID (*Alén's* [*a*-] *acid*), 1-naphthylamine-3:6-disulphonic acid, is obtained by nitrating naphthalene-2:7-disulphonic acid and reducing the product with ammonium sulphide or iron filings (Freund, G.P. 27346; *cf.* Friedländer and Taussig, Ber. 1897, **30**, 1462) or by boiling 1-naphthylamine-3:6:8-trisulphonic acid with zinc dust and alkali (G.P. 233934). Freund's acid gives 1- and other hydroxynaphthalene-3:6-disulphonic acids when heated with caustic alkali and is used in the manufacture of azo-dyestuffs.

FRIEDRICHS' EXTRACTOR (*v.* Vol. IV, 587*b*).

FRITILLARIA, ALKALOIDS OF. Three different species of *Fritillaria* have been investigated:

Fritillaria imperialis L.
PEI MU { *F. verticillata* Willd. and its var. *thunbergii*.
TA PEI { *F. roylei* Hook.

Fritillaria imperialis: An alkaloid *imperialine*, $C_{35}H_{60}O_4N$, was extracted from this plant by Fragner (Ber. 1888, **21**, 3284). Short needles, m.p. 254° (approx.); $[a]_D$ $-35{\cdot}4°$ (in $CHCl_3$). The alkaloid is said to be a heart poison and may be related to the older alkaloid *tulipine*, discovered by Gerard in *Tulipa gesneriana* L.

Pei Mu.—This interesting drug finds wide application in Chinese medicine and is prescribed in fevers, coughs, dysuria, hæmorrhages, lingering labour, rheumatism, and diseases of the eye. The main difficulty is to identify its botanical origin and Pei Mu was indeed attributed to *Fritillaria roylei* Hook (so-called Szechuan variety) by Stuart ("Chinese Materia Medica," 1911, 178) or to *F. verticillata* Willd. var. *thunbergii* Bak. (so-called Chekiang var. = Ta Pei) by Read and Liu ("Chinese Medicinal Plants," Peiping, 1936, 3rd ed.).

Ta Pei (Chekiang) is said to yield *peimine* (Chi, Kao and Chang, Amer. Chem. Soc. 1936, **58**, 1306), whereas *Pei Mu* (Szechuan) affords *verticine*, *verticilline*, *peimine*, *peiminine*, *fritimine*, and *fritillarine* (Chou and Chen, Amer. Chem. Abstr. 1932, **26**, 5703; 1933, **27**, 3033; Fukuda, Chem. Zentr. 1930, I, 988).

From *F. verticillata* Willd., Yagi (Arch. intern. Pharmacodynamie, 1913, **23**, 277) obtained *fritilline* and an amorphous base.

Verticine, $C_{18}H_{33}O_2N$ or $C_{19}H_{35}O_2N$, $[a]_D^{10}$ $-10{\cdot}6°$, m.p. 224–224·5°, needles from **EtOH**.

Verticilline, $C_{19}H_{33}O_2N$, crystals sintering at 130° and melting at 148–150°, which then solidify and remelt at 213°.

Fritillarine, $C_{19}H_{33}O_2N$, m.p. 130–131°, amorphous, isolated as perchlorate.

Peimine, $C_{19}H_{30}O_2N$ (?) (Chou and Chen) or $C_{26}H_{43}O_3N$ (Chi *et al.*), m.p. 223°, optically inactive, **B·HCl**, m.p. 295°; **B·HBr**, m.p. 293–294°; $B{\cdot}H_2SO_4$, m.p. 278–280°.

Peiminine, $C_{18}H_{28}O_2N$, $[a]_D^{24}$ $-62{\cdot}5°$, m.p. 135°, needles from alcohol and light petroleum, **B·HCl**, m.p. 295°; **B·HBr**, m.p. 292°.

Fritimine, $C_{38}H_{62}O_3N_2$, $[a]_D^{22}$ $-50°$, m.p. 167°, colourless plates from **EtOH** or acetone, **B·HCl**, m.p. 230°.

Fritilline, $C_{25}H_{41}O_3N,H_2O$, m.p. 214°.

For pharmacology of the fritillary bases, *see* Narumi (Amer. Chem. Abstr. 1935, **29**, 8132; 1936, **30**, 7211) and Chen, *et al.* (*ibid.* 1935, **29**, 4084).

Schl.

FROTH FLOTATION (*v.* Vol. III, 485*c*).

FRUCTOSE (*v.* Vol. II, 286*a*).

FRUCTOSIDASE (*v.* Vol. IV, 313*b*).

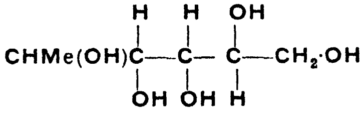
FRÜHLING'S EXTRACTOR (*v.* Vol. IV, 581*d*).

"*FUADIN*" *v.* CATECHOL (Vol. II, 432*d*).

FUCHSISENECIONINE, $C_{12}H_{21}O_3N$, an alkaloid of *Senecio Fuchsii*.

FUCITOL, $C_6H_{14}O_5$, is the pentahydroxy alcohol derived from galactomethylose (fucose), the pentose obtained from *Fucus vesiculosus*. The dextro, lævo and racemic isomers are all known.

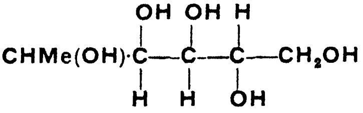
d-**Fucitol** [Fucitol],



$$\mathrm{CHMe(OH)}\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{CH_2{\cdot}OH}$$

may be prepared by reducing *l*-fucose [fucose] with 2·5% sodium amalgum in dilute sulphuric acid (Votoček and Potměšil, Ber. 1913, **46**, 3655, also Chem. Zentr. 1915, I, 605). It crystallises from alcohol in white silvery leaflets, m.p. 153–154°, $[a]_D^{20}$ $+4{\cdot}7°$ (·3991 g. fucitol in 13 c.c. of 10% aqueous borax solution).

l-**Fucitol** [Rhodeitol],



$$\mathrm{CHMe(OH){\cdot}}\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2OH}$$

may be prepared by reducing *d*-fucose [rhodeose] with sodium amalgam in weak alkaline solution (not exceeding ½% **NaOH**) (Votoček and Bulfř, Chem. Zentr. 1906, I, 1818). White plates, m.p. 153·5°. Distils without decomposition. Easily soluble in water, insoluble in alcohol, $[a]_D^{21}$ $-4{\cdot}6°$ in 10% borax solution.

It is not oxidised by sorbose bacteria, but has been oxidised with *Acetobacter suboxydans* (M. Hann, E. Tilden and C. Hudson, J. Amer. Chem. Soc. 1938, **60**, 1201).

dl-**Fucitol** [racemic rhodeitol; racemic fucitol] is prepared by reduction of *dl*-fucose with sodium amalgum (Votoček and Bulír, *l.c.*). It may also be obtained from equal quantities of fucitol and rhodeitol in alcohol (Votoček and Potměšil, *l.c.*).

It forms white plates, m.p. 168–170°, distils without decomposition, is soluble in water, and insoluble in alcohol.

Trityl Fucitol has been prepared by dissolving fucitol in dry pyridine and adding the calculated quantity of $ClCPh_3$. The trityl derivative is precipitated with water after a few days, m.p. 138–142°, $[a]_D$ $-5{\cdot}0°$ (F. Valentin, Coll. Czech. Chem. Comm. 1931, **3**, 499).

FUCOSE (*v.* Vol. II, 287*c*).

FUCOSOL. A mixture of furfurol and methyl furfurol derived from the pentoses of certain algæ by distillation with dilute sulphuric acid.

FUCOSTEROL (*v.* Vol. I, 199*c*).

FUCOXANTHIN (*see* CAROTENOIDS). The carotenoid pigment of brown seaweed (*Fucus vesiculosus*) was isolated by partition and chromatographic methods. It separates from ether—light petroleum in brown red prisms, m.p. 166–167°, analysis indicating the formula $C_{40}H_{60}O_6$. Whereas the living *Fucus vesiculosus* contains *β*-carotene and fucoxanthin, the dead material contains *β*-carotene and zeaxanthin.

No trace of the last pigment could be found in the fresh algæ; it is therefore suggested that a *post-mortem* transformation, fucoxanthin → zeaxanthin occurs.

The carotenoid contains four hydroxyl groups (Zerevitinov), but the function of the remaining two oxygen atoms has not been established. Oxidation of fucoxanthin gives dimethylmalonic acid and 4–5 mol. of acetic acid. Catalytic hydrogenation of the pigment yields a colourless substance $C_{40}H_{78}O_2$, m.p. 63–64°, which does not give a coloration with tetranitromethane. Fucoxanthin gives a royal blue coloration with hydrochloric acid and a blue coloration with antimony trichloride (Karrer *et al.*, Helv. Chim. Acta, 1931, **14**, 614; Heilbron and Phipers, Biochem. J. 1935, **29**, 1369).

I. M. H. and F. S. S.

FUEL. This term includes all combustible substances obtainable in bulk which may be burned by means of atmospheric air in such a manner as to render the heat evolved capable of being economically applied to domestic and industrial purposes. Fuels may be divided into (*a*) naturally-occurring or primary fuels, and (*b*) secondary or prepared fuels derived from (*a*), both groups containing solid, liquid and gaseous members. The general relationships between the primary and secondary fuels are shown in Table I.

TABLE I.

Primary fuels.	Secondary fuels.		
	Solid.	Liquid.	Gaseous.
Wood	Charcoal.		Producer-gas.
Peat	Peat-charcl.		
Lignite	Briquettes.	Lignite tars.	Producer-gas.
Coal	Semi-coke. Coke.	Motor spirit. Tars and oils.	Town-gas, coke-oven gas, producer-gas, water-gas, blast-furnace gas.
Anthracite	Briquettes		Producer-gas.
Oil, shale.		Shale oil.	
Petroleum		Motor spirit. Kerosene. Diesel oil. Fuel oil.	
Natural gas		Compression-gasoline. Synthetic fuels.	Compressed butane, etc.

The economic importance of a fuel depends upon (i) its geographical distribution; (ii) its cost of production, transport and storage in bulk; (iii) the total amount of heat obtainable by burning unit weight of it and (iv) the rapidity, efficiency and smokelessness of its combustion with atmospheric air. Of the natural fuels, coal is the most important, for despite the probability that there is more combustible matter in the peat deposits than in all the known coal-fields of the world and admitting the marked inferiority of coal to petroleum in calorific value, no other fuel combines so many economic advantages. Thus, in 1935, the approximate quantities of the most important fuels produced were: bituminous coal and anthracite 1,126, lignite 201 and crude petroleum 235 million metric tons respectively.

The calorific value of a fuel is expressed as the number of parts by weight of water which may be heated through one thermometric degree by the complete combustion of unit weight (unit volume in the case of gases) of the fuel under such conditions that the whole of the heat is transferred to the water, and that the products leave the system at atmospheric temperature and pressure. The metric unit of heat adopted for technical purposes is the kilogram-centigrade unit (K.C.U.) or the quantity of heat required to raise the temperature of 1 kg. of water through 1°C. in the neighbourhood of 15°C., while the British Thermal Unit (B.Th.U.) is the amount of heat required to raise the temperature of 1 lb. of water through 1°F. in the neighbourhood of 60°F. Thus, 1 K.C.U.=3·968 B.Th.U., 1 B.Th.U.=0·252 K.C.U., and 1 K.C.U. per kilo =1·8 B.Th.U. per lb. In dealing with gases, the calorific values of which are expressed on a volumetric basis, it is necessary to specify the conditions of temperature and pressure under which the unit volume is assumed to be measured. For scientific purposes, these conditions are 0°C. and 760 mm.: in British technical practice, the standard is 60°F., and 30 in. mercury, the gas being saturated with water vapour. For purposes of calculation it is often more convenient to express the calorific value of a gas as K.C.U. per g. mol. (=22·418 litres at 0°C. and 760 mm.) than in the more usual forms of K.C.U. per cu.m. or B.Th.U. per cu. ft. In such a case, x K.C.U. per g. mol.=46·68 x K.C.U. per cu.m. at 0°C. and 760 mm., or 5·02 x B.Th.U. per cu. ft. at 0°C. and 760 mm.

Seeing that all fuels contain hydrogen, a distinction is sometimes drawn between the *gross* and *net* calorific values, the former implying that *all* the products of combustion have been cooled to atmospheric temperature (15°C.), while the latter takes account of the fact that in practice it is not feasible to cool the products sufficiently to condense the steam produced on combustion, consequently neither the latent heat of condensation of the steam nor the sensible heat in the water between the temperature of condensation (assumed to be 100°C.) and room temperature can be considered as contributing to the calorific value of the fuel. A deduction of 11·196 K.C.U. per g. mol. of steam produced on combustion (=622 K.C.U. per kg. or 1,119·6 B.Th.U. per lb.) is therefore made. This deduction is, however, excessive, since the assumption is made that condensation would take place at 100°C. and that the water would then be cooled to 15°C., which is incorrect, since the partial pressure of the steam is below 760 mm.; the most that can justifiably be allowed is the latent heat of condensation of steam at 15°C., namely 588·7 K.C.U. per kg. of water (1,059·7 B.Th.U. per lb.) or 10·6 K.C.U. per g. mol., and this value has been used in calculating the net calorific values throughout this article.

The calorific value of a solid or liquid fuel is determined by burning a known weight of it in oxygen at a pressure of not less than 25 atm. in some form of bomb calorimeter, that known as the Berthelot-Mahler apparatus being well adapted for the purpose. In the hands of an experienced worker, the method is more accurate than any yet devised, provided that all the proper corrections (*e.g.* for radiation and for the formation of nitric acid) are properly determined and applied in each experiment. The " water equivalent " of the bomb and its accessories may be determined by burning in it a known weight of compressed benzoic acid. A comparison between the value so obtained and that calculated from the known weights and specific heats of its separate elements serves as a good test of the proper heat insulation of the bomb in the calorimeter, which is apt at times to become defective. Such a comparison should be made frequently as a precaution against possible error which might otherwise escape detection. With ordinary care duplicate determinations on the same coal sample should give results agreeing within 50 K.C.U., and when special precautions are taken within 25 K.C.U. on about 8,000 K.C.U. per kg.

It is evident from its construction that the bomb method gives the heat of combustion under " *constant volume* " and not under " *constant pressure* " conditions, but as the combustion of a bituminous or anthracite coal in oxygen is attended by very little change in gaseous volume (*e.g.* $C_9H_6O+10O_2=9CO_2+3H_2O$) the difference between the two values is perhaps negligible in practice. Strictly speaking, however, the necessary small correction ought to be applied to the " bomb " results in deducing the true " *constant pressure* " value.

The constant pressure value may be calculated from that at constant volume by the following formula:

$$Q_{cp}=Q_{cv}-(\triangle n)RT.$$

Q_{cp} and Q_{cv} are the calorific values at constant pressure and constant volume respectively, $\triangle n$ is the *increase* in the number of gaseous molecules after the reaction; R is the gas constant =1·9885 (or 2·0 with sufficient accuracy) and T is the absolute temperature at which the reaction is carried out.

The correction amounts in the case of bituminous coals to about 6–8 K.C.U. per kg. (10–14 B.Th.U. per lb.), and hence is less than the experimental error inherent in the determination. Though opposite in sign, it is in general about equal to the correction for nitric acid formed during combustion in the bomb. With fuels, such as petrol, which may contain about 15% of hydrogen, the correction may amount to about twice this value or (say) 15 K.C.U. per kg.

The calorific value of a gas is usually determined by burning a measured volume at atmospheric pressure in a chamber surrounded by a system of coils or the like, through which a flow of water at a constant head is maintained. By suitable regulation of the pressure and flow of gas and water supplies respectively, the gas may be completely burned and the heat developed transferred substantially without loss to the water, the products leaving the apparatus at a temperature only slightly above that of the atmosphere. A number of forms of this apparatus are in use, and of recent years several forms of recording gas-calorimeter have been adopted. For further details, *see* GAS, COAL, and C. G. Hyde and F. E. Mills, " Gas Calorimetry," 1932.

The heat of combustion of amorphous carbon is 8,080 K.C.U. per kg. when completely burned to the dioxide, and 2,417 when burned to the monoxide; recent values for a number of the principal constituents of gaseous fuels are given in Table II.

TABLE II.—CALORIFIC VALUES OF GASEOUS FUELS.

	K.C.U. per gram-molecule.		B.Th.U. per cu. ft. at 0°C. and 760 mm.	
	Gross.	Net.	Gross.	Net.
Hydrogen . .	68·4	57·8	343·0	289·8
Methane . .	213·0	191·8	1067·7	961·4
Ethane . .	373·0	341·2	1870·5	1711·0
Ethylene . .	336·6	315·4	1689·7	1581·4
Propylene . .	490·2	458·4	2457·8	2298·4
Acetylene . .	311·1	300·5	1559·8	1506·9
Carbon monoxide . . .	67·6		339·0	

The *gross* values for certain single liquid fuels in K.C.U. per kg. are *n*-hexane=11,518, benzene=10,044, toluene=10,174, methyl alcohol=5,429, ethyl alcohol=7,149. An increase of $>CH_2$ in ascending an homologous series of hydrocarbons or alcohols corresponds to an increase of approximately 158 K.C.U. in the gross heat of combustion per gram-molecule.

It is not possible to calculate accurately the calorific values of compound fuels such as coal or petroleum from their elementary compositions, since the heat of combustion of a compound is never equal to the sum of those of its elements taken proportionally. Numerous formulæ have been suggested to enable the calorific value of coal to be calculated from either the proximate or ultimate analysis. One of the best known is that of Dulong

$$Q=\frac{1}{100}\left\{8{,}080C+34{,}460\left(H-\frac{O}{8}\right)+2{,}250S\right\}$$

K.C.U. per kg., where **C**, **H**, **O** and **S** are the percentages of carbon, hydrogen, oxygen and sulphur respectively. The assumption is made that the contribution of each element to the calorific value of the coal is that which it would make were it in the free state, subject to the qualification that the oxygen in the coal is assumed to be combined as water with its quota of hydrogen, which hydrogen is therefore considered to make no contribution to the heating value of the coal. More recently, E. S. Grumell and I. A. Davies (Fuel, 1933, **12**, 199) have put forward a formula,

$$Q=(3{\cdot}635H+235{\cdot}9)\left\{\frac{C}{3}+H-\frac{1}{8}(O+S)\right\},$$

based on Berthier's suggestion that the heat evolved by a fuel is proportional to the air required for combustion.

Although the assumptions underlying these and similar formulæ are certainly not correct, the results are sometimes surprisingly close to those determined in a bomb calorimeter, particularly with coals the oxygen content of which does not exceed about 7·5% and where the carbon content is not above 92 or 93%. If the oxygen content much exceeds 7·5%, however, agreement between the " bomb " and calculated calorific values is likely to be poor. Unfortunately, no definite correlation appears to exist between oxygen-content and formula-error, either in magnitude or in sign.

On the other hand, since the properties of a gaseous mixture are additive in respect of its constituents, the heats of combustion of gaseous fuels can be calculated with a reasonable degree of accuracy (1 or 2%) *provided the relative proportions of the combustible gases, their nature and calorific values are accurately known.* These requirements are most satisfactorily fulfilled by gases of which the combustible constituents are only hydrogen, carbon monoxide and methane (water-gas, producer-gas and blast-furnace gas). Where, however, there are appreciable proportions of heavy hydrocarbons absorbable by bromine (coal-gas, carburetted water-gas and oil-gas), uncertainty is introduced as to the precise value which should be assumed for the heat of combustion of these compounds. It is often assumed that the heat of combustion of the heavy hydrocarbons is that of propylene. Hyde and Mills (*op. cit.*), however, have shown from the comparison of the determined and calculated calorific values of 34 samples of gas (the calorific values of which ranged from 410 to 604 B.Th.U. per cu. ft.) that the error introduced by this assumption may be from +2 to −21 B.Th.U. per cu. ft. with an average of −11·8, and that, in order to equalise the calorimetric and calculated results, the heavy hydrocarbons must be assumed to have heats of combustion ranging from 2,286 to 3,333 B.Th.U. per cu. ft. at 60°F. and 30 in. Hg, saturated at 60°F. The differences are likely to be accentuated when dealing with oil-gas and the gases from the low temperature carbonisation of coal, since not only are there greater relative proportions of unsaturated hydrocarbons higher than propylene, but the saturated hydrocarbons are mixtures of methane and higher homologues.

The so-called " calorific intensity " of a fuel is an unscientific term, inasmuch as the highest temperature which a particular fuel is capable of producing depends entirely upon circumstances which are to some extent indefinable and difficult of control. The idea that the calorific intensity of a fuel may be deduced by dividing its calorific value by the mean specific heat of the products is based on the assumptions (*a*) that the whole of the potential heat is instantaneously realised, and (*b*) that it appears without loss as sensible heat in the products of combustion. Neither of these assumptions is correct; combustion takes place in stages and its degree of completeness depends on the temperature realised in the flame (*i.e.* on the equilibrium constant proper to the flame temperature), assuming that equilibrium has been reached. Furthermore, the products of combustion (CO_2 and water vapour) radiate heat to an extent depending on the temperature of the flame, which heat does not appear as sensible heat in the products. A graphical method for determining flame temperatures of gaseous fuels has been developed by A. J. V. Underwood " Technical Data on Fuel," 1935, and readers are referred to this for further details. The measurement of furnace temperatures and the like (Pyrometry) is, however, of great practical importance and many instruments have been devised for this purpose.

A. Solid Fuels.

1. NATURAL FUELS.

Coal.—All natural solid fuels have originated in woody tissue which consists principally of cellulose $n(C_6H_{10}O_5)$, and lignin (about $nC_{36}H_{42}O_{14}$), together with smaller proportions of proteins, resins, fats and waxes. The view is generally, though not universally, held that the fossil solid fuels, peat, lignite, coal and anthracite, represent stages in the progressive transformation and degradation under the combined influence of increasing pressure and also possibly of temperature, of debris derived from the vegetation of primeval forests and swamps. This process has gone on in most of the great geological periods, and, so far as its early stages are concerned, it is being repeated to-day under somewhat different conditions in our modern peat-bogs and deltas, where enormous masses of water-logged vegetable debris are decomposing under the influence of bacteria. A consideration of the geographical distribution of the world's principal coal-fields shows that all the important fields adjacent to the North Atlantic and Arctic areas (which include nearly all the fields of North-West Europe and in the eastern part of North America) originated in what geologists call the Carboniferous Period of the Primary Era; what may be termed the " Indian Ocean " group of coal-fields (which include those of China, India, Australia and South Africa) originated somewhat later in the same period. Mesozoic coals are found in the interiors of North America and Asia (intra-continental group); while Tertiary coals are chiefly found in what may be termed the Pacific borderland (west of North America, Japan and New Zealand) as well as in regions bordering on the Gulf of Mexico and the Mediterranean.

The great coal-fields of the Carboniferous System lie in a broad belt, stretching round the world almost in a great circle, and probably originated in a new monster vegetation flourishing in a rich virgin soil, with an equable if not subtropical climate, and large areas of shallow sea to which great quantities of sediment were borne from rivers. According to G. Hickling, the microscopic examination of Carboniferous coals has shown that they have originated predominantly from wood and bark.

Vegetable tissue has been built up in all ages, then as now, by the action of chlorophyll under the influence of sunlight, stimulated by minute quantities of mineral salts drawn in by the roots, upon atmospheric carbon dioxide and moisture. An action which sets up a complex series of chemical changes, with the intermediate formation of sugars and starches, ultimately resulting in the production of celluloses and lignocelluloses, as the basis of all woody tissue.

The vegetable forms which flourished in the Carboniferous Period were of simpler structure, but of much greater size, than those which are predominant to-day—lepidodendrons, sigillarias, gigantic ferns, club mosses, horsetails and forms intermediate between ferns and cycads—and it is demonstrable that in certain cases (*e.g.* the Moira seam near Loughborough in Leicestershire) entire beds of coal have been formed from the spores of such plants, which were produced and shed in great profusion.

Much controversy has raged round the question whether or not coal formation has occurred upon the actual site of the original vegetable growth, and in many cases the question can be answered affirmatively. The necessary conditions would be a dense forest growth in swampy areas, together with such oscillations in level as are known to have occurred during the Carboniferous Period. During a period of subsidence, the rotting vegetable debris would be overlaid by water-deposited sands and clays, which, on re-elevation, would provide a suitable soil for renewed vegetable growth. Proof of such conditions is afforded by the occurrence of "under-clays" or fireclays with fossil roots (stigmaria) below the coal seams in certain areas (*e.g.* the Yorkshire coal-field), and, speaking generally, our British coal-fields would appear to have been formed *in situ*. On the other hand, however, some coal-fields undoubtedly owe their origin to enormous masses of vegetable debris brought down from higher levels and deposited either in deltas or in landlocked seas or lakes. Such fields show no fossil roots in the understrata, and sometimes fossil remains of aqueous and marine life are found immediately above and below the coal seams.

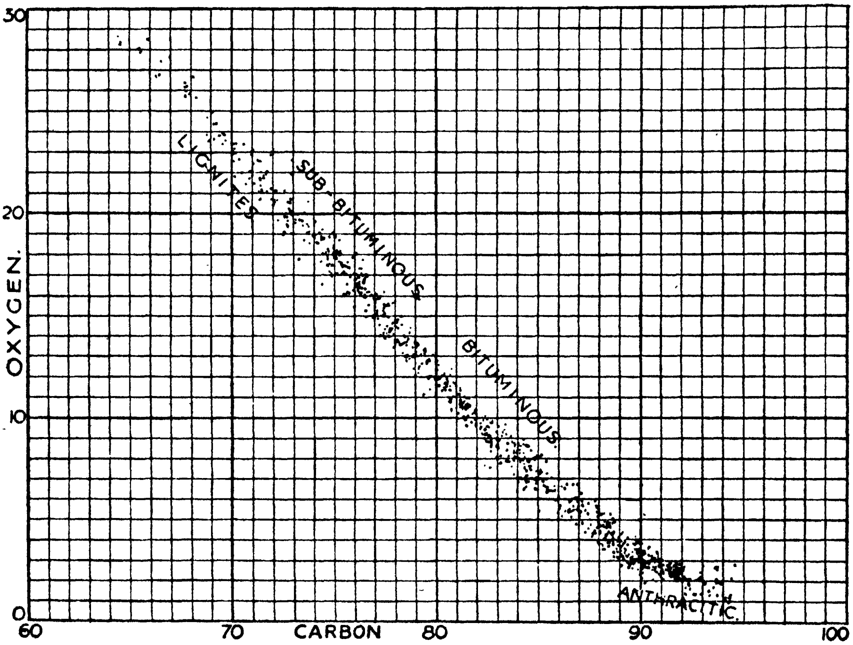


FIG. 1.

Although the transformation process cannot be visualised in all its details, its general outline may be pictured as involving such successive stages as (i) fermentation in peat-bogs, whereby the less resistant parts of the vegetable tissue would be decomposed; (ii) progressive consolidation and de-watering of the residue by pressure as it was gradually "blanketed" under accumulating newer strata; (iii) lamination produced by subsequent earth movements; and (iv) what, for want of a better word, has been termed "bituminisation" under the combined influence of increasing pressure and in a subordinate degree of slowly rising temperature. This latter probably did not exceed (if ever it approached) 200°C., except in the rare cases where bituminous coals have been subsequently subjected to such influences as igneous intrusion or frictional heat generated by earth movements. Such "bituminisation" seems to have involved *inter alia* a loss not only of both carbon dioxide and water, as the result of intra-molecular condensations, but also of methane, as well as a condensation of acidic and basic intermediate "humic" bodies from lignins and proteins resulting ultimately in the "coal substance" of a matured bituminous coal. Researches now proceeding at the Imperial College are affording evidence of the potency of high pressure in effecting such condensations. In the course of all these transformations and maturing processes substances have been gradually formed, probably through intermediate bodies of a phenolic type, which ultimately gave rise to the coking propensities of bituminous coals.

It seems probable that during the peat-bog stage some portion of the fermented residue would be reduced to a condition of colloidal solution, which, on subsequent slow evaporation in drying, would give rise to a gel, while the more complex and resistant part would remain admixed with, or suspended in, water. Such supposition, which is supported by experimental work in the research laboratories of the Imperial College, might perhaps account for the alternate bands of bright vitreous and dull constituents found in many bituminous coals. However that may be, it is highly probable that, during the fermentation and maceration of the original debris which characterised the peat-bog stage, a considerable amount of segregation of the various molecular aggregates would take place through the agency of water, according to their complexities. Such changes would necessarily involve both great shrinkage in bulk and loss of weight in the original vegetable debris; thus it has been demonstrated that the existing coalfields represent about 20–28% only of the original weight and one-tenth only of the bulk, of the original woody tissue from which they were formed.

The normal outline of coal formation, so far as it is known to-day, may perhaps be epitomised in some such provisional diagram as the following:

OUTLINE OF COAL FORMATION.

Original Material.

Lignocelluloses.
Vegetable proteins.
Resins, fats and waxes.

↓

(1)

(*a*)	(*b*)	(*c*)
Fermentation. Peat bog with evolution of $CH_4+CO_2+H_2O$	***Maceration.*** by water, and possibly also *Segregation* giving (*a*) colloidal solutions (gels), (*b*) insoluble matter.	*Transportation*[1] by water and redeposition elsewhere.

↓

(2)

(*a*)	(*b*)
Blanketing under newer strata and *consolidation* and *de-watering* of the mass by pressure.	*Earth movements* producing laminated structure.

↓

(3)

Bituminisation.

under influences of pressure and (subordinately) slowly rising temperature.

(*a*) Progressive de-watering.
(*b*) Loss of CO_2 and H_2O by internal condensations and of CH_4.
(*c*) "Amalgamation" of acidic and basic humic bodies.
(*d*) Development of coking constituents from phenolic bodies.

↓

(4)

Anthracitisation.

under influence of pressure and temperature produced by intensive earth movements.

The continuity of the peat → lignite → coal → anthracite series is supported by graphical analyses of coal-composition data made both by O. C. Ralston in 1915 (U.S. Bur. of Mines Tech. Paper No. 93), and by G. Hickling in 1926 (J. Inst. Fuel, 1932, **5**, 326). Thus, for example, on plotting against each other the percentages of carbon and oxygen in the "dry ashless" organic substance of a large number of coals of all types and classes, Hickling obtained the diagram shown in Fig. 1, which (as he said) affords "an almost complete proof of the view that the long range of types of normal fossil fuels (excluding cannels, bog-heads, etc.) have all been developed by the progressive alteration of essentially similar masses of plant deposit." And further support has been forthcoming from researches at the Imperial College (Proc. Roy. Soc. 1935, A, **148**, 492) upon the development of benzenoid structure in the peat → coal → anthracite series, a point which is further considered on p. 355*d*. An alternative to the orthodox view, based upon the examination of a large number of coal-seams, has been advanced by McKenzie Taylor (Fuel, 1928, **7**, 66, 127, 227). He found that under certain kinds of clay-type roofs, base exchange has taken place between roof material and sodium chloride in the original vegetable material, whereby the alkalinity of the maturing coal has been preserved so that ærobic decay has resulted in the ultimate successive formation of bituminous coals and anthracites. But in the absence of such base exchange, acid anærobic decay has resulted in the transformation of peat ultimately into brown coals and lignites which, under such conditions, he considers are incapable of further maturing to bituminous coals. Other investigators, while accepting the essential continuity of the peat → lignite → coal series, have suggested that it does not extend to anthracites. However, it would be difficult to exclude certain

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[1] Only, however, in cases where the subsequent coal formation did not take place on the original site of growth.

TABLE III.—ULTIMATE ANALYSES OF TYPICAL PRODUCTS IN THE WOOD TO COAL TRANSFORMATION.

Material.	Original.		Irish Peat.	Brown coals.			Lignites.			Sub-bituminous, Nigerian.	Bituminous, Yorks., Barnsley.	Anthracite, Welsh.
	Wood.	Lignin. $C_{10}H_{12}O_3$.		Rhenish.	Italian, Valdarno.	Australian, Morwell.	Canadian, Saskatchewan, brown.	Canadian, Alberta, black.	Malayan, black.			
Percentage water in raw material .	—	—	90	60	40–50	55	37·8	16·0	20	10	2·5	1·0
Percentage ash in dry material . .	1·25	—	5·0	7·5	7–10	4·0	7·65	9·0	6–10	7·5	2·75	3·0
Dry ashless material:												
C	50·0	66·65	60·2	64·3	60·3	65·1	67·75	72·6	73·0	75·0	84·7	92·0
H	6·0	6·65	5·5	5·85	5·4	5·0	4·30	4·2	5·5	6·0	5·1	3·0
N and S	1·5	—	2·0	0·9	1·95	0·5	1·55	2·6	1·5	2·4	2·2	1·0
O	42·5	26·70	32·3	28·95	32·25	29·4	26·40	20·6	20·0	16·6	8·0	4·0
C/H ratio	8·33	10·0	11·0	11·0	11·15	13·0	15·5	17·3	13·3	12·5	16·6	30·7
Percentage volatiles at 900°C. . .	75	—	65	55·9	57·8	57·6	45·0	40·3	46·5	45·0	33·0	Below 8

examples in which anthracitisation of bituminous coals has undoubtedly occurred in consequence of subsequent igneous intrusion or heat generated by intensive earth movement.

Although the organic substance of bituminous coals invariably contains small percentages of both nitrogen and sulphur—which presumably originated in vegetable proteins—its chief progenitors are generally regarded as celluloses and/or lignins; but opinion is sharply divided as to which of these two classes of organic material have been mainly responsible. Thus, while F. Fischer (Ges. Abhd. Kohle, 1919, 4, 342; 1920, 5, 135, 160, 200, 211, 235; 1921, 6, 1) and his collaborators maintain that during the "peat-bog stage" the celluloses in the original vegetable debris were decomposed leaving only the lignin to be subsequently transformed into coals, Berl (J. Inst. Fuel, 1932, 5, 382) has argued, from his work on the "coalification" of plant products by heat under pressure, that while lignins may have been the chief progenitors of brown coals and lignites, celluloses have been mainly responsible for bituminous coking-coals. And he doubts whether bituminous coals have matured via brown coals and lignites, as is usually supposed.

Assuming, however, the essential continuity of the wood → peat → coal → anthracite series, the sequence of the various intermediate products may be represented as follows:

THE WOOD → PEAT → COAL → ANTHRACITE SERIES.

Woody tissue
↓
Peats (Quaternary) {Water = 90; Combustible = 10} ↓ Woody brown coals
↓
Earthy brown coals (Tertiary) {Water = 60 to 40; Combustible = 40 to 60}
↓
Laminated lignites {Water = 40 to 20; Combustible = 60 to 80}
↓
Sub-bituminous coals {Water = 20 to 10; Coal = 80 to 90}
↓
Bituminous coals {Water = 10; Coal = 90}
↓
Semi-bituminous coals
↓
Anthracitic coals

From the ultimate composition of typical products in the series shown in Table III, it will be seen that, generally speaking, while both the carbon-content and the C/H ratio increase, the oxygen-content and yield of volatiles at 900°C. diminish with the maturity of the coal-substance.

Wood when dry consists chiefly of cellulose and from 20 to 25% of lignin together with about 4% of sap, associated with a small amount of mineral ash (chiefly $CaCO_3$ and K_2CO_3).

Recently felled timber contains a large proportion of water (from 26 to 50%), the percentage depending upon the season when the tree was felled and the part of the tree examined. When air-dried the moisture may range between 12 and 15%; kiln-drying may reduce it to as little as 5%. Timber is classed as "hard" or "soft" wood according as it is derived from trees with broad leaves or conifers (narrow-leaved). As a fuel, wood is very combustible, and burns with a great amount of flame, but it suffers from the disadvantage that the calorific value, even when dried, is low (from 4,710 to 5,085 K.C.U. per kg.), the higher values being for woods containing much resinous matter such as fir and pine. It is well adapted for domestic use and is also employed for firing boilers, its low ash content making it a clean fuel without clinkering properties. Owing to the large content of hygroscopic water, it is quite unsuitable for the attainment of high temperatures, unless it is first carbonised (charcoal) or gasified in a producer. On distillation in closed retorts or chambers it yields under favourable conditions, 20–25% of charcoal, 9–13% of tar, 40–50% of pyroligneous acid (corresponding to 2–4% anhydrous acetic acid), and 22–23% of inflammable gases. The chief timber-producing countries are the U.S.S.R. with 1,566 million acres of forests, Canada with 739 million acres, the United States with 600 million acres; other countries with important timber reserves are India, Northern Rhodesia and Nigeria, with 180, 113 and 99 million acres respectively.

According to the "Statistical Yearbook (1936)" of the World Power Conference, the five countries which used the greatest quantities of wood as fuel in 1934 were: Germany (including the Saar), Poland, Nigeria, Tanganyika and Uganda, which consumed 35·8, 13, 13·6, 20 and 10 million cu. m. respectively.

The rapid demolition of the world's reserves is becoming a serious economic problem, and while it is improbable that wood will ever again take an important rank as a fuel, nevertheless, in countries which are deficient in natural sources of liquid fuels, efforts are being made to employ wood or charcoal instead of petrol to operate lorries.

Peat is a widely distributed and abundant fuel of great future potentiality, but is as yet of little economic importance. It is usual to distinguish between bog peats to which the smaller forms of vegetation are the main contributors, and forest peats, mainly formed from trees. Peat-bogs are principally found in high latitudes; one-seventh of Ireland is covered with them, while in Great Britain about 6 million acres are so covered to an average depth of about 12 ft. Extensive deposits also occur in Russia, Scandinavia, northern Germany, Bavaria, Austria, Italy and northern France, as well as in Canada and Siberia. Forest peats, to which most Carboniferous coals may be referred, occur chiefly in the dense forests of the tropical and sub-tropical rain belts.

Peat deposits vary considerably in age, the oldest peats having a dark-brown or black colour, with but merest traces of the original vegetable structure, while the more recent varieties are light-brown in colour, of spongy texture, with distinct vegetable structure. They contain a fairly large and variable proportion (5–15% as a rule) of mineral matter usually of an infusible character, composed of sulphates and carbonates of calcium and magnesium, ferric oxide and silica. Fuchs estimates that high-moor peats accumulate at the rate of about 1 metre in 1,000 years, and their age may exceed 5,000 years.

A well-drained peat bog contains about 90% of water and only 10% of combustible matter. Although about 90% of the water can be pressed out mechanically in the cold, the residue is a gel still containing as much water as combustible material, and it must be heated to 150–200°C. before the remainder of the water can be expressed.

"Air-dried" peat still contains from 15 to 25% of water; its calorific value varies between about 2,250 and 4,300 K.C.U. per kg., with an average of about 3,000 K.C.U. per kg. Dry ashless peat usually contains:

C 50–64, H 4·7–6·8, O 28–44 and N 0·5–2·5%.

its sulphur content being low.

Generally speaking, the deeper the peat lies in a deposit the higher its carbon- and the lower its oxygen-contents, though there may be irregularities. According to Fuchs, as the peat matures pentosans diminish more rapidly than celluloses.

Oden and Lindberg, who analysed a large number of continental peats, found that their proximate compositions (dry) varied between the following limits:

	Per cent.
Waxes and resins . . .	0·2– 3·7
Celluloses	3·5– 9·5
Humic and pectinic acids .	21·0–27·0
Lignins.	15·0–71·0
Residues	7·6–21·0

Although the use of air-dried peat as a domestic fuel is very ancient, progress has been slow and in most cases so dependent on laborious hand-winning methods that as yet peat has attained no great importance as a general fuel, its employment being restricted to localities near which it naturally occurs. Many attempts have been made—notably in Germany, Sweden and Canada—to develop mechanical methods both for the excavation and spreading of peat, for its de-watering either by the application of heat and/or pressure or by electro-osmosis. But while mechanical excavation has met with some success, no processes have yet been commercially established for the mechanical or electrical de-watering of peat. The problem is to produce blocks of briquettes containing not more than from 15 to 30% of water from raw peat containing about 90%; this means the elimination of at least 95% of the original water-content, and to do so by heat alone would involve the combustion of more than the whole peat substance.

Reliable statistics as to the utilisation of air-dried peat in various countries are difficult to obtain and such as are available can only be regarded as approximate. In Russia it may possibly now amount to as much as 10 million tons, in Ireland to 7 million tons, in Germany to 3 million tons and in Denmark and Sweden to between 1 and 3 million tons per annum. From 1908 onwards, the Canadian Department of Mines has carried out extensive experiments on peat production and utilisation, and has issued several valuable Reports thereon by B. F. Haanel (1912 and 1914), A. von Anrep (1914) and a Committee in 1922 and 1926. In 1926 the U.S. Bureau of Mines published a comprehensive Report on the " Commercial Utilisation of Peat " (Bull. No. 253), while H.M. Fuel Research Board has issued Reports on " The Peat Resources of Ireland " (1920), " The Winning and Utilisation of Peat in Ireland " (1921) and " The Production of Air-dried Peat " (1922). The Canadian Committee concluded (1922) that the then cost of producing a ton of air-dried peat fuel containing 30% of moisture, based on 100 working days of 10 hours each per annum, would be $4·48, which might possibly be reduced to $3·5 with a 20-hour day; the corresponding costs at that time in Denmark and Germany were estimated at less than $2·25 per ton. By 1928 the cost in Canada is said to have fallen to between $2·5 and $3·0 per ton.

In 1921 the Fuel Research Board carried out some carbonising tests at 820–1,000°C. on air-dried Turraun Irish peat containing (as charged) 20% of water, the results of which were published in Technical Paper No. 4.

Although peat containing up to 60% of moisture has been gasified on a large scale in gas producers under ammonia-recovery conditions, for successful commercial working the moisture-content should not exceed 30%. The richness of the gas depends upon the moisture-content, but where this is not excessive, the " total combustible " in the gas may amount to between 35 and 40%, as in the following typical example:

CO_2 20·0, CO 10·0, H_2 23·2, CH_4 4·8 and N_2 42·0%.

It would seem probable that a ton of *dry* peat should be capable of yielding up to 90,000 cu. ft. of gas of an average gross calorific value 140 B.Th.U. per cu. ft., though part thereof would be required to raise steam for working the ammonia-recovery plant.

With regard to power-production via gas-producers and internal combustion engines, trials made by the Canadian Department of Mines in 1910–11 at the Fuel Testing Station, Ottawa, showed at full load a consumption of 1·7 lb. and at three-quarters load 2·1 lb. of *dry* peat per B.H.P. hour.

At the Wiesmoor Electric Power Station in Ostfriesland, Germany, the capacity of which was increased after the war of 1914–18 to 21,000 kw. and where the boilers, which supply steam to the turbo-generator, were partly coal-fired (30,000 tons per annum) and partly peat-fired 60,000 tons per annum), the best consumption obtained with air-dried peat was 4·85 lb. (2·2 kg.) as compared with a best consumption of 2·65 lb. (1·2 kg.) of coal per kw. hour, the average peat-consumption being 6·6 lb. (3·0 kg.) per kw. hour.

According to information given at the World Power Conference in 1928, the use of specially-designed shaft chain-grate furnaces with air-blast pre-heated to 350°C. has enabled air-dried peat containing 35–38% of moisture to be so effectively burnt under boilers that already peat-fired electric power stations of a total capacity 612,000 kw. were either working or in course of erection in the U.S.S.R. Among these may be mentioned Shatura (115 km. from Moscow), with an initial capacity of 48,000, but designed for ultimate extension to 100,000 kw., Leningrad of 110,000 kw. ultimate capacity, Nijni Novgorod and Lyopino. In 1928 the total production of peat in Russia was 7 million tons, of which 5½ million tons were for industrial and 1½ million tons for domestic purposes. Indeed it has been claimed that " the problem of economically burning peat in the U.S.S.R. has been satisfactorily solved, since peat (low-grade fuel as it is) has been burned with as high a calorific efficiency as the highest grade fuel," and certainly in Russia large-scale electric power generated from air-dried peat may be regarded as an established process.

Brown Coals, Lignites and Sub-bituminous Coals.—Brown coals and lignites comprise a large class of chiefly Tertiary coals, occurring (i) in what may be termed the Pacific borderlands (*i.e.* in America west of the Rockies, Japan, Australia, New Zealand and the East Indies), (ii) in India, Burma and Malaya, (iii) in regions adjacent to, and in continuation with, the Gulf of Mexico (*i.e.* Texas, Mississippi, Arkansas and Alabama), (iv) in regions north of the Mediterranean, including the Central European Plain, and finally (v) in a large area in the United States and Canada (comprising North and South Dakota, Montana, Wyoming, Saskatchewan and Alberta) in which coal-forming conditions prevailed during the Cretaceous Period and were continued in great luxuriance into the subsequent Tertiary Era. In the last-named area there are immense reserves of brown and black lignites in the Tertiary and of sub-bituminous coals in the Upper Cretaceous formations, and great seismic movements consequent upon the elevation of the Rockies after the coalfield was laid caused local bituminisation and even anthracitisation of the fields.

Owing to their comparatively recent origin, brown coals and lignites are mostly found near (or not far from) the surface, so that they can be won at no great cost by either open workings or shallow mining. Moreover, they include a great variety of fuels which may be generally subdivided, according to their external characters and maturities, into: (1) earthy brown coals, *e.g.* the Australian Morwell brown coal; (2) woody brown coals (*e.g.* the Italian Valdarno brown coal), which have a marked woody structure, as though they had never passed through any " peat-bog " stage, but had merely become " fossilised " during complete submergence under water; (3) laminated lignites, mainly black in colour, with a conchoidal fracture which, though quite devoid of coking properties, nevertheless (as will be shown later) are sufficiently matured to show the incipient formation of constituents which when fully developed in bituminous coals are mainly responsible for

TABLE IV.—PROXIMATE AND ULTIMATE COMPOSITIONS OF TYPICAL BROWN COALS AND LIGNITES.

Coal.	(1) Australian, Morwell, earthy brown coal.	(2) Italian, Valdarno, woody brown coal.	German.		Western Canadian.				(9) Bikanir, woody brown lignite.	(10) Burmese, black lignite.	(11) Malayan black lignite.
			(3) Rhenish, earthy brown coal.	(4) Saxon, brown lignite.	(5) Estevan, brown lignite.	(6) Cardiff, black lignite.	(7) Rose Deer, black lignite.	(8) Harlech, black lignite.			
Per cent. water as received	55	40–50	59·1	[15·1][1]	37·8	18·0	16·0	6·9	16·1	19·4	20·0
Per cent. ash in dry coal	4·0	7–10	5·2	11·0	7·65	11·7	9·0	8·8	11·0	4·85	6–10
C	65·1	60·30	66·35	70·05	67·75	71·2	72·6	76·0	72·15	67·45	73·0
H	5·0	5·40	4·85	5·45	4·30	4·3	4·2	4·3	5·50	4·75	5·5
N } S	0·5	1·95	1·00	0·55	0·95	1·7	2·0	1·2	0·50	1·15	1·5
S				4·70	0·60	0·5	0·6	0·5	3·15	0·35	
O	29·4	32·35	27·80	19·25	26·40	22·3	20·6	18·0	18·70	26·30	20·0
Per cent. volatiles at 900°C., on dry ashless coal	57·6	57·8	54·6	60·1	44·9	41·3	40·3	36·0	56·9	50·35	46·5
Per cent. Montan wax extractable from dry coal	less than 0·5	—	2·8	6·0	←	less	than 0·5	→	5·1	0·3	2·35
C/H ratio	13·0	11·1	13·7	12·9	15·7	16·5	17·3	17·7	13·1	14·2	13·3

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[1] Partially dried before receipt.

their coking propensities. It will be seen that (2) is a special class, out of line with the other two; and there are border-line classes between (1) and (3).

The raw coals contain from 60 downwards to 20% of water, according to their maturity, the expulsion of which usually causes disintegration, and from 0 up to about 7·5% of Montan wax (m.p. usually 78–88°) and sometimes other bodies of vaseline-like consistency extractable by boiling benzene under atmospheric pressure. When present in sufficient amount these useful incidental constituents render the dried coals compressible into briquettes without addition of any extraneous binder. Montan wax is usually a mixture of higher fatty acids and their esters with (possibly) higher hydrocarbons. Four such waxes extracted from German brown coals in the course of researches at the Imperial College (Proc. Roy. Soc. 1934, A, **147**, 58), melted between 80 and 85°C., and had empirical formulæ approximating to $C_nH_{2n}O_2$, where $n = 29–32$.

Proximate and ultimate compositions of a series of typical brown coals and lignites are given in Table IV.

From the point of view of utilisation, brown coals and lignites suffer from several inherent disadvantages, (i) their content of water is high, and when dried they tend to disintegrate, giving much fine dust, (ii) even when dried, their calorific values are low (5,800–7,000 K.C.U. per kg. on the dry ashless coal), and (iii) owing to the very high yield of volatile matter, they burn with long smoky flames. Notwithstanding these disadvantages, however, brown coals and lignites are successfully employed for steam raising, notably in Germany and Austria, while it may be mentioned that the electricity supply of the city of Melbourne is derived from the Yallourn (earthy brown) coal of the Latrobe Valley (*see* "The Utilisation of Brown Coal in Victoria," Empire Mining and Metallurgical Congress, Montreal 1927).

W. A. Bone (Proc. Roy. Soc. 1921, A. **99**, 236), showed that by heat treatment of dry brown coals and lignites at temperatures below 400°C. considerable condensation of their cellulosic or humic constituents may be effected, with simultaneous elimination of oxygen as oxides of carbon (mainly CO_2) and water, but without expulsion of either hydrogen or hydrocarbons. As a result of this treatment the dry ashless coal substance loses from 8 to 15% in weight while at the same time, practically the whole of the potential energy of the fuel is concentrated in the residue.

The sub-bituminous coals form a somewhat ill-defined class of (chiefly) Cretaceous coals intermediate between the lignites and the bituminous coals. They usually contain from 10 to 20% of water and are devoid of coking properties. They are well matured fuels, in external appearance more of lignitic than bituminous type, but in ultimate composition they approximate to the lowest grade of the latter. In the dry ashless state they usually contain between 75 and 80% of carbon, and from 10 to 20% of oxygen, and at 900°C. yield about 45% of volatiles.

Bituminous, semi-Bituminous and Anthracitic Coals.—The term "bituminous" is applied to a whole series of matured flaming coals of Carboniferous and Mesozoic origin, including all types of coking coals, the commercial importance of which exceeds that of all other kinds.

They are all outwardly black in colour, with often a banded appearance, a laminated or columnar structure with a tendency to cubical fracture, and they usually soil the hands. Generally speaking, the ultimate composition of the dry ashless coal falls between the following limits:

C 75–90, **H** 4·5–5·5, **N** 1·0–1·5, **S** 1·0–2·0 and **O** 5–20%.

The yield of volatiles at 900°C. varies between 18 and 45%.

The chief coal-producing countries are, and have been for many years, the United States, Great Britain and Germany, which have produced upwards of 65% of the annual world output of black coal. Figures for 1913, 1929 (when the peak of coal-production was reached) and 1935 are given in Table V.

TABLE V.—WORLD'S PRODUCTION OF BLACK COAL.

	Million metric tons.		
	1913.	1929.	1935.
United States . .	508·7	543·6	381·3
Great Britain . .	287·4	258·0	226·5
Germany (post-1919 territory, including the Saar) . . .	152·1	174·2	144·7
Other countries .	246·8	327·8	373·5
Totals . . .	1,195·0	1,303·6	1,126·0

The average net costs of production per ton of commercially disposable coal in Great Britain in 1913 and 1935 were 9*s*. 5½*d*. and 12*s*. 11¾*d*. respectively, while the amount of coal raised per person employed had risen from 260 to 289 tons per annum. At the same time, the average consumption per head of population fell from 89 to 72 cwt. The reduction in demands for British coal since 1918 is to be ascribed mainly to three factors: (i) reduction in foreign exports (to the extent of about 33 million tons per annum in 1935 as compared with 1913) arising from the intensive development of coalfields in continental countries which previously imported large quantities of coal, (ii) the extensive adoption of liquid fuels by the mercantile marines and navies of the world and, (iii) progress in fuel economy the effect of which probably amounts to a reduction in internal demands for coal of upwards of 25 million tons per annum. A detailed discussion of the economic aspects of the British coal industry is given by W. A. Bone and G. W. Himus in "Coal, Its Constitution and Uses," Longmans, 1936.

A comprehensive report on the coal resources of the world was issued by the International Geological Congress in 1913, according to which the total probable and possible reserves of coal of all kinds (anthracite, bituminous coals and lignites) within 6,000 ft. of the surface amounted to 7·4 million million metric tons, or about 5,500 times the present total annual consumption. Although revised estimates have since been put forward, notably for the reserves of China, which appear to have been much over-estimated, no comprehensive survey has since been made. According to the 1913 report, of the total world reserves, 6·75% are anthracites (mainly in China), 52·75% are bituminous, and 40·5% are sub-bituminous (lignites and Tertiary brown coals); 51·8% occur in the United States, 16·4% in Canada, 13·5% in China, 5·7% in the pre-1914 German Empire, 2·6% in Great Britain, 2·3% in Siberia, and 21·2% in Australia. South America and Africa are relatively devoid of coalfields.

CLASSIFICATION OF COAL.

For commercial purposes, coals are classified according to their suitability, or otherwise, for certain specific economic ends, *e.g.* steam raising, furnace firing, gas making, manufacture of dense metallurgical coke and the like. The usefulness of any given coal for a particular purpose depends principally upon (i) its yield of volatiles expelled at 900–1,000°C., which largely determines the length and character of the flame produced during vigorous combustion; and (ii) the character of the carbonaceous residue after the volatiles have been expelled at high temperature, which doubtless depends in part upon the nature and mode of decomposition of the "binding" constituents of the coal. For economic purposes, Percy proposed to class bituminous coals as (i) non-caking, free-burning, rich in oxygen; (ii) caking; and (iii) non-caking, rich in carbon. Several classifications have been proposed based upon the ultimate composition of the dry and ashless coals. One of the most useful is that generally known as the Regnault-Grüner which is shown in a modernised form in Table VI. This classification has been criticised in that it is based largely on the oxygen-content of the coal, which bears all the analytical errors, and also that it underrates the importance of hydrogen. C. A. Seyler, as the result of a special study of the coals of South Wales, has put forward a chemical classification based upon the percentages of carbon and hydrogen in the pure coal substance. He divides coals into five principal genera, according to their hydrogen contents; each genus is then sub-divided into a number of species according to the percentage of carbon. The classification which is detailed in Table VII thus really depends on two factors, namely, in the first place upon the hydrogen content, and in the second upon a **C**/**H** ratio.

The Geological Survey of the United States, independently of Seyler's work formerly also adopted a classification based upon the **C**/**H** ratio in the pure coal substance. Of recent years, however, a classification, shown in Table VIII, based upon the proximate analysis of the ashless raw coal and its physical properties, has been adopted.

TABLE VI.—THE REGNAULT-GRÜNER CLASSIFICATION OF COALS (AS REVISED BY W. A. BONE AND G. W. HIMUS).

Genus.	Class.	Chief uses.	Percentage composition.			Per cent. volatiles at 900°C.	Per cent. fixed carbon.	Character of carbonaceous residue.
			C.	H.	O+N+S.			
A. Lignites.	Non-caking.	—	60–75	about 5·0	20–35	about 45	below 55	Non-coherent.
B. Bituminous.	[1] Non-caking long flame.	Reverberatory furnaces.	75–80	4·5–5·5	15–20	40–45	55–60	Non-coherent.
	[2] Caking long flame.	Gas making.	80–85	about 5·6	10–15	32–40	60–68	Very porous coke.
	[3] Hard coking.	Coke manufacture.	84–89	5·0–5·6	5·5–11·0	26–32	68–74	Dense coke.
	[4] Hard coking short flame.	Coke manufacture and steam raising.	88–90	4·5–5·5	5·5–6·5	18–26	74–82	Very dense coke.
B.C. Semi-bituminous.	Non-caking short flame.	Steam raising.	90–92	4·0–4·5	4·0–5·5	15–20	80–85	Weakly caking or non-coherent.
C. Anthracitic and anthracites.	[1] Anthracitic non-caking.	Steam raising.	92–94	3·0–4·0	3·0–4·5	8–15	85–92	Pulverulent.
	[2] Anthracites non-caking.	Domestic and central heating; malting kilns.				below 8	above 92	

All the numerical data in the above table refer to the dry ashless coal.

TABLE VII.—SEYLER'S CLASSIFICATION OF COAL.

Carbon plane.	Anthracitic.	Carbonaceous.	Bituminous.			Lignitous.	
			Meta-.	Ortho-.	Para-.	Meta-.	Ortho-.
Carbon.	Over 93·3%.	93·3–91·2%.	91·2–89·0%.	89·0–87·0%.	87·0–84·0%.	84–80%.	80–75%.
Per-bituminous genus.	—	—	Per-meta-bituminous. North country steam coals.	Per-ortho-bituminous. Cannels.	Per-para-bituminous. Cannels.	Per-lignitous.	—
H over 5·8% . .	—	—	Over 5·7	Over 5·7	Over 5·8	Over 5·8	
Vol. 30–44% . .	—	—	30–44	Seldom under 36	Seldom under 40	31–57	—
Bituminous genus.	—	(Pseudo-bituminous species.)	Meta-bituminous. Welsh coking coals.	Ortho-bituminous. Durham coking coals. Smithy and gas coals.	Para-bituminous. Many of the best gas coals, coking coals and free-burning steam coals.	Lignitous.	—
H 5·0–5·8%	—	5·0–5·8	4·9–5·7	5·0–5·7	5·0–5·8	4·7–5·8	
Vol.	—	Over 23	23–30	23–30	30–40	31–57	
Semi-bituminous genus.	—	Semi-bituminous species. (Ortho-semi-bituminous.) Generally coke. Caking index increases with hydrogen content. Steam coals.	Sub-meta-bituminous. Continental coking coals.	Sub-ortho-bituminous. Best Westphalian coking coals.	Sub-para-bituminous.	Sub-lignitous.	—
H 4·5–5·0% . .	—	Over 4·45	4·5–4·9	4·5–5·0	5·0 and under.	—	—
Vol. 16–23% . .	—	14–24	16–23	16–23	16–29	—	—
Carbonaceous genus.	Semi-anthracitic species. Dry (non-coking) steam coals.	Carbonaceous species. (Ortho-carbonaceous.) Welsh smokeless steam coals, slightly coking.	Pseudo-carbonaceous. (Sub-meta-bituminous.) steam coals.	Pseudo-carbonaceous. (Sub-ortho-bituminous.)	Pseudo-carbonaceous. (Sub-para-bituminous.)	Sub-lignitous.	—
H 4·0–4·5% . .	Over 4	4·2–4·5	3·7–4·5	Over 4·5	—	—	—
Vol. 10–16% . .	9–15	10–14	10–16	Over 16	—	—	—
Anthracitic genus.	Ortho-anthracite. True anthracites.	Pseudo-anthracite. (Sub-carbonaceous.) Dry steam coals. Bastard anthracites.	Pseudo-anthracitic. (Sub-meta-bituminous.)	Pseudo-anthracitic. (Sub-ortho-bituminous.)	Pseudo-anthracitic. (Sub-para-bituminous.)	—	—
H below 4·0% .	Below 4·0	Below 4·2	Below 3·7	—	—	—	—
Vol. under 10% .	5–9	Under 7·7	Under 10	—	—	—	—

C. A. Seyler, " Fuel in Science and Practice," III, 15–26, 41–49, 79–83 (1924).

TABLE VIII.—ANALYTICAL LIMITS AND PHYSICAL CRITERIA FOR VARIOUS RANKS OF COAL.

(According to the U.S. Geological Survey and Bureau of Mines.)

Rank.	Equivalent term.	Proximate analysis on ash-free basis.				Physical properties and occurrence.
		Moisture, %.	Volatiles, %.	Fixed carbon, %.	Calorific value on ash-free basis. B.Th.U. per lb.	
A.	Peat.	90–80	—	—	—	Peat.
B.	Lignite.	50–32	25–30	28–37	6,400–8,300	Slacks freely on weathering; non-coking; northern part of Great Plains and Gulf Coastal area.
C.	Sub-bituminous.	32–12	32–38	36–50	8,550–11,000	Slacks considerably on weathering; non-coking; western states and possibly certain coalfields of Iowa, Illinois, Missouri, Western Kentucky and Indiana.
D.	Bituminous, low rank.	12–5	39–42	49–53	12,000–13,600	Slight or no slacking on weathering; may be coking; all coal-bearing states except the Dakotas.
E.	Bituminous, high rank.	5–35	40–22	55–75	14,000–15,000	No slacking properties; often coking; most abundant in Appalachian field, but found in most coal-bearing states.
F.	Semi-bituminous.	26–23	23–15	74–82	15,200–15,300	Friable; coking; nearly smokeless; Central Pennsylvania; New River Pocahontas field; Fort Smith field of Arkansas and Oklahoma.
G.	Semi-anthracite.	Fuel ratio (F.C./V.M.) from 4·0–10·0.				Less hard and less lustrous than typical anthracite; near Lykens, Bernice and Carbondale in Pennsylvania; Meadow Branch field of West Virginia; and Valley field of Virginia.
H.	Anthracite.	All Pennsylvania anthracite with fuel ratio over 10·0.				Pennsylvania anthracite.
I.	Super-anthracite.					Resembles graphite; Rhode Island and Southern Massachusetts. Local deposits due to metamorphism caused by volcanic dykes and sills.

Although, as already stated, in Carboniferous bituminous coals the density of the coke yielded at 900°C. and upwards usually increases progressively as the yield of volatile falls, a point is reached (somewhere between 15 and 18% volatiles) at which the coking propensities abruptly disappear and the coals pass into the non-caking short-flame steam-raising class; this includes all the famous "admiralty" steam-coals occurring in the central portion of the South Wales coal-field (*v. infra*). In the dry ashless state they usually contain

C 90–92, **H** 4·0–4·5, **O** 3·0–4·5, **N** and **S** 1·5%

and yield between 15 and 20% of volatiles at 900°C. They are all first-class steam-raising coals burning well in a good draught with a short smokeless flame.

There is much evidence in support of the view that these semi-bituminous coals have been formed through the action of heat, arising from either seismic movement or later igneous intrusion, upon seams that were originally bituminous.

The anthracitic genus comprise coals containing in the dry ashless state upwards of 92% of carbon, and yielding less than 15% of volatiles at 900° and they may be sub-divided into:

(i) *Anthracitic.*—Hard steam coals yielding at 900° between 8 and 15% of volatiles, devoid of caking properties and burning smokelessly with a short non-luminous flame. They usually have a low content of infusible ash. As a typical example, a coal from a seam in the Main Colliery Company at Neath in South Wales of the following composition may be cited:

C 89·05, H 3·90, N 0·40, S 1·00, O 5·65%.

(ii) *Anthracites* are coals yielding less than 8% of volatiles at 900°C. In Great Britain they are found for the most part in the west and north-west border of the South Wales coal-field (West Glamorgan, Breconshire, Carmarthenshire and Pembrokeshire) over an area of 137,000 acres, and to a small extent in certain localities in Scotland (Ayrshire, Linlithgow and Fife), where the bituminous seams have been subjected to intrusion of molten igneous material subsequent to the formation of the original coal-field Nearly 80% of the world's reserves of anthracites are said to be located in China, and there are also extensive fields in Russia and the United States (Pennsylvania).

Anthracites are usually distinguished by their very low ash-content and comparative freedom from sulphur; owing to their cleanliness and smokeless combustion they are used chiefly for domestic heating in specially constructed closed stoves, for central heating furnaces, for drying malt, curing rubber, and other special purposes where a smokeless fuel of great purity is required. The advantages of anthracite for domestic heating are more appreciated on the Continent, where closed slow-combustion stoves are largely used, than in England where the open fireplace is the rule.

A typical example of a Scottish anthracite, from Manor Powis near Stirling, contained C 92·5, H 3·2, N 1·8, S 0·9, O 1·6% on the dry ashless coal.

THE GEOGRAPHICAL DISTRIBUTION OF COAL.

British Coal-fields.—The coal-fields of Great Britain may be grouped into three principal areas, each having distinctive features, namely: (*a*) *Southern* (South Wales, Forest of Dean, Bristol and Kent); (*b*) *Central* (Lancashire and North Wales; Yorkshire, Derbyshire and Nottinghamshire; Leicestershire; Staffordshire and Warwickshire); and (*c*) *Northern* (Durham and Northumberland, Cumberland and Scotland). The more important fields are as follows:

(1) *South Wales* (Monmouth, Glamorgan, Carmarthen and Pembrokeshire), covering an area of about 1,000 square miles, of which 150 are under the sea, with seams from 1 to 12 ft. (average 2·5–3·0 ft.) thick, and yielding all classes of coal, namely, bituminous (31%), steam coals (47%), and anthracites (22%). The Carboniferous strata lie in an elongated basin which is almost completely surrounded by older formations, and complicated towards the south by an anticlinal fold running east and west. The basin is much faulted, and the rivers have cut a series of deep valleys along which the coal seams crop out. Speaking generally, and for corresponding depths below the surface, there is a gradual transition in the character of the coal from the coking varieties in the east and south-east, through the first-class steam coals of the centre, to the semi-anthracites and anthracites in the west and north-west. The supposition that the anthracitisation has been due to prior bituminous seams having been subjected to heat generated by an increasing earth pressure has been questioned by Strahan and Pollard, "Memoirs of the Geological Survey," 1908, who, from the fact that the ash-content of the anthracites is invariably much lower than that of the bituminous seams which are their continuation, suggested that the difference between the two classes of coal may be due to some original disparity in the vegetable debris from which they have been derived, but no proof of it has yet been forthcoming and, taken as a whole, chemical evidence is against it. In the eastern and south-eastern sections of the field, the upper and middle parts of the measures are chiefly worked, yielding good coking and bituminous coals; in the central sections, the middle parts of the measures (the Pennant Series) preponderate, whilst in the extreme west the seams occur in lower parts of the measures only. The percentage composition of the more important classes of coals usually falls within the following limits:

LIMITING COMPOSITIONS OF THE MORE IMPORTANT CLASSES OF SOUTH WALES COALS.

Class.	C.	H.	O. and N.	S.	Ash.	Volatiles.
Anthracites.	91·0–93·0	3·0–3·7	1·9–3·5	0·7–1·0	0·7–1·7	5·0–6·0
Steam .	85·0–90·0	4·0–4·7	3·5–4·5	0·7–1·5	2·0–3·3	7·0–20·0
Bituminous (coking).	80·0–95·0	5·0–5·5	—	—	—	20·0–25·0

The estimated reserves amount altogether to 26,000 million tons, of which 6,310 million tons are anthracite and 3,936 million tons semi-bituminous steam coals. In good years the production of the field has exceeded 50 million tons, but in 1933 it was only 33⅛ million tons.

(2) *Forest of Dean.*—A small field (34 sq. miles) forming a complete basin between the Wye and Severn valleys, and containing thirty-one seams, of which only sixteen exceed 1 ft. in thickness. It is usually regarded as an outlier of the South Wales coal-field. The total thickness of the measures is 2,765 ft., and they are completely girdled by older formations. The coals resemble in character those found in the eastern section of the South Wales field; the upper and middle parts of the measures yield excellent gas and house coals, whilst the lower parts which, however, are difficult to work owing to accumulations of water therein, contain good steam coals. The total estimated reserves in the field are 258 million tons, and the annual production since 1918 has varied usually between 1 and 1·5 million tons, the maximum having been 1·438 million tons in 1923.

(3) *Bristol* (Somerset and Gloucester).—The coal-fields of this region form a number of basins of varying areas, the edges and outlines of which are masked by newer rocks, so that there are five or six detached exposed fields, in all about 2590 sq. miles, and a considerable intervening area of concealed coal-fields. The measures are divided into upper and lower portions by a sandstone bed, some 2,000–2,500 ft. in thickness, known as the Pennant Rock, which, although it contains locally some thin coal seams, is practically unproductive. The upper parts of the measures (the Radstock and Farrington Series) yield bituminous house and gas coals; the lower part (Kingswood and Vobster Series) yield both house and coking coals. The combined annual outputs of the various fields is comparatively small, and is almost all consumed locally. The Kingswood Great Vein coal contains:

Moisture 1·6, ash 4·1, **C** 81·8, **H** 4·7, **N** 1·4, **S** 0·9 and **O** 5·5%.

The estimated reserves amount to 4,198 million tons, and since 1918 the annual production has varied usually between 1·0 and 1·5 million tons, the maximum being in 1920.

(4) *East Kent.*—A concealed coal-field near the East Kent coast, now known to have an area of 206 sq. miles (namely 150 on land and 56 under the sea), was first proved in 1886 by an experimental boring at Shakespeare's Cliff, Dover, where coal measures were encountered at 1,100 ft. below the surface. It is generally considered as a westward prolongation of the coalfields in Belgium and Northern France, and to have originated contemporaneously with those of South Wales, Gloucester and Somerset. The Kent coal measures, of which between 4,700 and 4,000 ft. have been proved, consist of greyish sandstones, shales and fireclays with numerous coal seams. The coal measures lie concealed below chalk and other Upper Cretaceous formations between which and the Palæozoic floor a wedge of Lower Cretaceous and Jurassic rocks has (so to speak) been introduced in a south-west to north-east direction. The coals, which are all bituminous and similar to those of Somersetshire, are being worked at the Tilmanstone and Snowdown collieries, and at the latter have the following proximate compositions: moisture 0·8–1·7, ash 2·5–7·5, fixed carbon 63–75, sulphur 1·0–1·3, volatiles 21–28%. At Tilmanstone, the raw coal from the "Five-Foot Seam" contains about 1% of moisture and about 6% of ash, and the dry ashless coal contains: **C** 85·0, **H** 5·0, **N** 1·2, **S** 2·4 and **O** 6·4% with **C**/**H** 17·0. It has been estimated that the total reserves exceed 2,000 million tons, and in 1933 the output was 1·928 million tons.

(5) *Staffordshire*, divided into (*a*) North Staffordshire (100 sq. miles), and (*b*) South Staffordshire (150 sq. miles). In the *North Staffordshire* area the sequence of upper, middle and lower coal-bearing measures underlain by the Millstone Grit and Carboniferous Limestone is complete although much broken by faults. With the exception, however, of two seams which have been worked along the eastern boundary in the lower portions of the measures, all the principal workable seams (fourteen in number) occur in the middle portions of the measures and most of them average 6 ft. in thickness. They yield good coking as well as gas, house and furnace coals. Some of the seams are worked in conjunction with the Black Band ironstone found in the coal measures in this area. The reserves are estimated at 4,500 million tons, and the annual outputs since 1918 have usually varied between about 5·5 and 6·5 million tons.

The *South Staffordshire* area is divided by a fault into a northern and a southern section. The northern section contains some fourteen workable seams in the middle portions of the measures; towards the south the measures thin out considerably and a number of the individual seams are found to have converged, finally forming the once famous Dudley Ten-Yard Seam. Neither Millstone Grit nor Carboniferous Limestone occur below the coal-bearing measures. The coals include both gas, house and furnace varieties; neither steam nor hard coking coals are found. In places the coals have been damaged by igneous intrusions such as that of Rowley Regis. The total reserves are estimated at about 1,415 million tons and the annual outputs since 1918 have usually varied between 1·4 and 2·0 million tons.

(6) *Warwickshire.*—This coal-field comprises an area of about 60 sq. miles in the north and north-east of Warwickshire, between Tamworth, Nuneaton and Coventry, in which the sequence of the Carboniferous rocks is the same as that found in South Staffordshire (*q.v.*). The total thickness of the productive measures is greatest in the north, where also the individual seams are most numerous; towards the south the measures get thinner and some of the separate seams converge to form much thicker ones, as in South Staffordshire. The coals are generally oxidised and, therefore, non-coking, with a high percentage of volatiles. The reserves are estimated at about 1,125 million tons, and since 1918 the annual outputs have mostly varied between 4·5 and 5·3 million tons.

(7) *Leicestershire.*—The exposed coal-field in north-west Leicestershire covers an area of about 30 sq. miles, beyond and around which, however, the coal measures continue for another 54 sq. miles as a concealed field under later Triassic rocks. Unlike the coal-bearing measures in South Staffordshire and Warwickshire, those of Leicestershire are underlain by Millstone Grit and Carboniferous Limestone. The coals are free-burning and similar in type to those of Warwickshire. The estimated reserves are 1,825 million tons and the annual outputs since 1918 have usually varied between 2·0 and 3·2 million tons.

(8) *Yorkshire, Derbyshire and Nottinghamshire.*—This, perhaps the largest of all our British coalfields, comprises an area of 808 sq. miles of exposed and 1,328 sq. miles of concealed measures. The exposed measures stretch in an unbroken line for a distance of 65 miles from Leeds in the north to Nottingham in the south, the breadth being about 23 miles at its maximum towards the north, and about 10 miles at its minimum near the southern end. Throughout the area the sequence of the Carboniferous

System is complete, and coals have nowhere been affected by igneous intrusions. The upper measures have been proved in boring operations under the New Red Sandstone, but they are everywhere unproductive of coal. The chief workable seams nearly all belong to the middle parts, although one or two important seams occur in the lower parts of the measures. The coals are highly bituminous, with from 25 to 45% of volatiles, and, although varied in character, are nearly all of high-grade quality. Some of the best English house and gas coals, as well as good coking and steam coals, are derived from the different seams in this field. Speaking generally, most of the seams found north of Sheffield have marked coking properties, although none of the coals yields so good or hard a metallurgical coke as do the famous Durham coking coals. South of Sheffield the coking properties of the coals diminish, but their gas-making qualities improve. In the southern part of the field (Notts.) the seams have apparently been oxidised, and although the coals obtained from them yield a large amount of gas, they are non-coking. The concealed measures extend eastwards from the exposed measures and include (in Yorkshire) collieries adjacent to the L.N.E.R. main line between Bawtry, Doncaster and Selby. Full reports have been made by the Fuel Research Board on the " Barnsley," " Beeston," " Deep Hard," " Parkgate " and " Silkstone " seams in this field.

The field is the most prolific of all British coal-fields, in 1929 and 1932 the outputs were 76 and 62 million tons respectively. After satisfying all requirements in its own area it exports house coals to London, gas coals to Birmingham, coke and coking coals to the blast furnaces at Scunthorpe and Frodingham (Lincs.) and steam coals abroad.

(9) *Lancashire.*—An irregular area, much faulted and broken by an east to west anticline, extending from Burnley in the north to Ashton-on-Lyne on the south (with a long tongue projecting southwards through Stockport to Macclesfield), and from Oldham in the east to St. Helens in the west. The total exposed area is about 500 sq. miles. The principal seams in the southern and central areas of the field are all found in the middle parts of the measures, the upper parts nowhere containing workable seams. The seams in the lower part of the measures become important in the northern districts in the neighbourhood of Accrington and Burnley. The coals from the seams in the middle parts of the measures belong almost exclusively to the gas-coal class and generally contain from 30 to 35% of volatiles. Several of these seams, notably the Yard Mine, Arley and Trencherbone, yield a fairly good coking coal. The famous 'Mountain Mine " seams occurring in the lower parts of the measures (Burnley and Accrington) yield coals containing from 26 to 27% of volatiles, which produce a coke almost, if not quite, equal to the best Durham coke. The Fuel Research Board has published detailed reports on the " Arley," " Mountain Mine," "King," "Ravine," "Smith" and Wigan Four-Feet seams in this coal-field. The reserves in the exposed field have been estimated at 4,238 million tons and contain the deepest workings in Great Britain (*e.g.* reaching 3,500 ft. at Pendleton Colliery, near Manchester). Its outputs since 1918 have varied between 13 million and 20 million tons per annum, mostly for consumption within its own borders; but the mining industry has been depressed sympathetically with the cotton trade of Lancashire.

(10) *North Wales* (Flintshire and Denbighshire).—This field (area=82 sq. miles) is similar in character to the Lancashire field. All the workable seams, however, are in the middle parts of the measures. The coals are similar in character to those occurring in the southern and central portions of the field; they contain from 33 to 35% of volatiles, and yield a fair quality of coke. The reserves are estimated at about 1,750 million tons and since 1918 the annual outputs have usually varied between 2·5 and 3·5 million tons.

(11) *Durham and Northumberland.*—In the great northern region of which Durham and Northumberland form an important part, there is a development of coal seams (more strongly marked the farther north) in the equivalent of the Carboniferous Limestone, a feature which is absent in the Midland and Southern fields. The total area of the field is about 800 sq. miles. In the Limestone Series there are a few workable seams which increase in number and thickness from south to north, but in the main part of the field the coal occurs chiefly in the middle parts of the measures. The southern and western districts of Durham probably produce the finest coking coals in the world, yielding from 22 to 28% of volatiles and comparatively small amounts of sulphur or ash. The central district (Sunderland to Newcastle) produces fine qualities of gas and house coals. The Northumberland seams are for the most part oxidised; they contain a rather large amount of moisture and are non-coking. They are largely used for steam coals, and they are excellent as gas-producer coals. The Fuel Research Board has issued detailed Reports on the " Main " and " Yard " seams in Northumberland, and the " Brockwell " and " Hutton " seams in Durham.

The area supplies coking coals and coke to the Tees-side and Cleveland blast furnaces and supports within itself great shipbuilding and engineering industries. It exports gas coals to the London gas works and steam coals abroad. The total reserves are estimated at 12,000 million tons and since 1918 the annual outputs have usually varied between 40 and 52 million tons, being 52·5 million tons (maximum) in 1929 and 40 million tons in 1932–33 (minimum), except for the two strike years, 1921 and 1926.

(12) *Cumberland or Whitehaven Coal-field.*—The area of this field is 150 sq. miles, and the character of the coals is in general similar to those obtained from the northern districts of Durham. The reserves are estimated at 1,527 million tons and the annual outputs since 1918 have usually varied between about 1·4 and 2·4 million tons.

(13) *Scotland.*—The coal-fields of Scotland extend in a relatively narrow strip from the east of Fife to the western sea-board at Ardrossan and Ayr, and occupy parts of the counties of

Fife, Clackmannan, East, Mid and West Lothian, Stirling, Lanark, Dumbarton, Renfrew and Ayr. In contrast with the English coal-fields, in which the workable seams occur almost entirely above the Millstone Grit, Scotland is the fortunate possessor of two coal measures, the one above and the other below the Grit; and, particularly in the East, the lower or Carboniferous Limestone measures are very productive. In Fife, in the small but highly mineralised Lothian area, and under the wide estuary of the Forth, there exist large resources of coal in these Limestone measures. A recent and authoritative estimate credits some of the eastern collieries with resources equivalent to two or three hundred years' production at the present rate of output, and, in one favoured instance, a thousand years' supply is computed to be within reach. The greater part of the output consists of various kinds of bituminous coals, the remainder being anthracite and cannel. Most of the bituminous coal is non-coking and is sold for steam raising, gas making, and household purposes. Valuable coking coals with a *caking index*[1] above 16, occur, however, in a restricted area of the Lower Coal Measures occupying the north-east fringe of the central coal-field, and extending over parts of the counties of Stirling, Lanark and Dumbarton. The resources of coking coal in that district are increased by the inclusion of coals with an index between 11 and 16 and of a character that makes them suitable for blending with the true cokers. Anthracite and semi-anthracite are mined chiefly in an expanse of the Lower Coal Measures lying to the east of Stirling, and a small amount of anthracitic coal is raised in other districts. Invariably it is associated in Scotland with igneous sills that have been injected between the coal-bearing rocks—intrusions that increase the difficulties and uncertainties of mining and not infrequently render the seams worthless. Good splints and cannels are also produced. North of the Tweed a *splint* is a hard coal which splits readily along the bedding planes and with difficulty in any other direction. It contains a considerable proportion of dull coal (*v.* p. 351*a*). Splints are perhaps the most characteristic of Scottish coals; they are used for steam raising, furnaces, bakehouses and as house coal; their calorific value is high, and they are robust and therefore satisfactory for shipment. Scotland also yields more varieties of *cannel* or *parrot* coal than any other region of these islands, if not of the world. Though of little present value they are again being sought for and tested with a view to utilisation for oil retorting, for which purpose some of them have special advantages in regard to the volume and quality of the oil they yield. Generally speaking, the bituminous coals of Scotland are high in volatiles, high in moisture and low in sulphur. Of recent years, electric power stations in densely populated districts, such as the London stations, have become constant buyers of Scottish coal in order to take advantage of its twin merits of reasonable price and low sulphur content. The total reserves have been estimated as follows:

Coal-field.	Million tons.
Fifeshire and Clackmannan .	4,186
Central (including Lanarkshire)	2,604
Ayrshire	1,082
Midlothian	2,500
Dumfriesshire	453
Underseas	2,443
Total	13,268

Since 1918 the annual outputs have usually varied between about 28 and 38 million tons.

Coal-fields of Germany (and Poland).—Before 1919 the principal Carboniferous coal-fields of Germany were those of (i) Upper Silesia, (ii) the Ruhr, and (iii) the Saar, as follows: (i) *Upper Silesia* (districts of Ratibor, Beuthen, Zabrze, Königshütte, Laurahütte and Pless). The Measures are 600 metres deep with seams 3–4 metres thick. The best coking coals are found near Zabrze eastwards, from which they gradually change into young gas coals near Königshütte, and finally into non-coking flaming coals near Laurahütte. (ii) *The Ruhr basin*, stretching from the neighbourhood of Hamm in the north-east to the Rhine in the south-west. The field is much broken by faults, and the Older Measures, which yield the best coking coals, are, as a rule, uppermost. The Middle Measures yield gas coals, and the Lower Measures non-coking varieties. The coals of the Ruhr basin contain 84–97% of organic matter, of which C 83·1–87·1 and H 5·27–5·68%. (iii) *The Saar district*. The Upper and Middle Measures are both thin and yield non-coking and flaming coals, the Lower Measures are thick, and yield (especially the deepest) very good caking and coking coals. The ash in Saar coals varies between 1·5 and 4·5% as a rule, occasionally running up to 7·7%. The carbon varies between 70 and 84%, and the hydrogen between 4·6 and 5·2%.

Coal-fields of the United States.—The chief coal-producing States arranged in descending order of productivity are as follows:

(1) *Pennsylvania* has two distinct coal-bearing areas, one bituminous and the other anthracitic. The bituminous regions in the west of the State contain all grades of steam, gas making and domestic coals. Among these, in Fayette County, is the Connellsville in the Pittsburgh bed, with an ash content less than 10% and volatile matter averaging 30%, while the sulphur rarely exceeds 1%, and nitrogen averages 1·50%. The coke from the Connellsville coal is greatly valued as a metallurgical fuel. The anthracite is in the north-east of the State. In 1929 the production of anthracite was 65,900,000 tons, and of bituminous coal 128,200,000 tons.

(2) *West Virginia* includes a large portion of the Central Appalachian region, which provides high-grade steam coals, some of which are suitable for coking. The coal beds are a continuation of the Pittsburgh bed in Pennsylvania in Brook and Fayette Counties. Analyses show C 74–86, H 4·0–5·2, N 1·0–1·7, S 0·5–1·2, ash 4·6–11·3%, and calorific values=13,736–15,190

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[1] The caking index is the number of grams of sand that can be bound by one gram of coal into a coherent lump containing not more than 5% of powder.

B.Th.U. per lb. In Harrison County, still in the Pittsburgh bed, coal is found containing on an average 4% of sulphur, with volatile matter about 40%, and ash 9·1%. In 1929 the production was 123,600,000 tons.

(3) *Illinois* includes the greater part of the eastern interior coal region, which extends from Rock Island and Wilmington (Ill.) in the north to central Kentucky in the south and from the Mississippi river in the west to Williamsport (Ind.) and Cannelton in the east. The coal is rather low grade and weakly coking, containing **C** 54–76, **H** 4·5–5·3, **N** 0·8–1·2, **S** 1·3–4·5, **O** 12·0–18·5, ash 12·0–24·0%, calorific value =9,929–11,907 B.Th.U. per lb. The proximity of the field to Chicago and St. Louis enhances its economic importance. In 1929 the production was 54,200,000 tons.

(4) *Kentucky.*—The eastern part includes part of the Central Appalachian Coal Region (*v.* (2) *West Virginia*) and part of the eastern interior field in the west. Both the eastern and western regions yield good steam and coking coals, the eastern region being, in this respect, superior to the western: the coke of the western region has too high a sulphur content to be of much use as a metallurgical fuel. In 1929 the production of Eastern Kentucky was 41,100,000 tons, and of Western Kentucky 12,900,000, or a total of 54,000,000 tons.

(5) *Ohio.*—The coal-fields are in the eastern part of the State, occupying the territory between the shore of Lake Erie in Geanga and Lake Counties south-west to Scioto and Lawrence Counties on the Ohio river. Approximately one-third of the State contains coal-bearing rocks. These fields occupy the western rim of the great Appalachian trough. This trough extends 850 miles south-west from Northern Pennsylvania to Central Alabama and has a maximum width of 180 miles. The Ohio fields contain 11 coal beds. The coals are of a good steam-class with high sulphur content. In 1929 the production was 21,180,000 tons.

(6) *Indiana* includes the eastern section of the eastern interior coal-field (*v.* (3) *Illinois*). Three kinds of coal are found: " block," cannel, and bituminous. During the period 1914–18 the production reached a maximum of 26,800,000 tons, but since then it has declined until in 1929 it became 16,380,000 tons. The coal is good for power production in large central power-plant, for railway, gas making and domestic uses.

(7) *Alabama* includes the Appalachian coal region of which the Warrior field is the greatly expanded southern end, and the main productive part includes the four counties Jefferson, Walker, Tuscaloosa and Fayette. Its known area is computed at 4,000 sq. miles, while the probable area is believed to be greater than this. The Cahaba is a narrow field extending north-east to south-west, and is separated from the Warrior field by the Birmingham Valley. Its area is about 350 sq. miles. The Coosa field is south-east of the Cahaba field, separated from it by the Cahaba Valley. The Plateau field is less well defined, being in part the north-westward continuation of the Warrior field. The entire area is estimated at 3,000 sq. miles. Over 99% of the coal mined is from the Cahaba and Warrior fields and serves for steam-raising, coking, railways and domestic heating. Over 85% of it is consumed within the State. About 35% of the annual output is coked in by-product ovens, the bulk of the coke being consumed in the blast-furnaces of the Birmingham district. In 1929 the total production was 16,200,000 tons.

(8) *Virginia.*—The Virginian coal regions are much scattered. They are the south-west Virginian fields, the Valley fields, and the Richmond basin. They include part of the Great Appalachian bituminous to semi-anthracite field. The beds are tilted and the workable area is small. The coal has long been mined. A considerable tonnage is shipped by water to New York and to New England ports. The higher grades from the south-west fields are much esteemed as steam coal. In 1929 the production was 11,390,000 tons.

(9) *Colorado.*—This is the most important coal-producing State west of the Mississippi; the coal is a black lignite, which rapidly disintegrates on exposure to air, so that it will not stand transport satisfactorily. In 1929 the production was 8,850,000 tons.

(10) The *Kansas and Missouri* coal-fields are in the eastern part of the State, while the most important deposits lie on the Kansas–Missouri boundary. The major part of the Kansas production is used for steam raising. It is a good locomotive fuel and the railways are its largest single consumers. " Dead coal " mined along the outcrop is much in demand for zinc smelting because of its non-coking properties. There is heavy competition from natural gas, and also from coal from Oklahoma and Arkansas. In 1929 the total output was 6,250,000 tons.

(11) *Wyoming* contains more coal than any other State. The coals range from low-rank sub-bituminous to high-rank bituminous. The coal formations in Wyoming are Cretaceous and Tertiary in age, and are usually broad synclinal basins lying between mountain ranges. Estimates by the U.S. Geological Survey show the amount of coal available as 599 million tons, an inexhaustible supply of low- and medium-rank coal. Wyoming has been a pioneer in the development of mechanised mining and has led all other States since 1928. The bulk of the coal is consumed by the railways, with domestic consumption next in importance. In 1929 the production was 5,985,000 tons.

(12) The *Tennessee* coal-fields are in two district areas, the north-eastern field and the main Cumberland Plateau field. In the former there are sharp-crested ridges reaching elevations of 3,500 ft. above sea level. Contrasted with this, the Cumberland Plateau field is a broad upland rising to 2,000 ft. above sea level. The coal of the Tracy City district yields good coke, while the Bon Air districts give excellent domestic and steaming grades. The greater part of the coal mined comes from the north-eastern field. In 1929 the production was 4,830,000 tons.

(13) The *Arkansas and Oklahoma* coal district is known as the Spadra. It contains the Hartshorne seam which is of Carboniferous age.

(14) *Utah.*—Carbon County is the source of more than 90% of the coal mined in Utah. The coal is high grade bituminous, and is excellent

as a domestic and steam-raising fuel; most of it can be ignited with paper without wood kindling. The coal from Castlegate is a good coking variety. In 1929 the production was 4,610,000 tons.

(15) *Iowa.*—The coal-bearing beds belong to the Pennsylvania series of the Carboniferous System. The Des Moines river flows south-east and cuts through the coal series. Iowa coal is low-grade and non-coking bituminous, carrying considerable sulphur in the form of pyrites (FeS_2) and gypsum. Iowa coal is used for locomotives, domestic purposes and power production. There is a good deal of competition from Illinois. In 1929 the production was 3,790,000 tons.

(16) *Montana* fields are distributed through the plains in the eastern and northern areas of the State, and the mountain regions in the central, southern and south-western parts of the State. Most of the Montana coal is used as railway fuel; some is consumed for domestic purposes and for smelting. The production in 1929 was 3,040,000 tons.

(17) *Maryland.*—The coal-fields lie in the western part of the State (Allegany and Garrett Counties) and are an eastern outlier of the main Appalachian coal-field. The major part of Maryland production is used for steam-raising, and lesser quantities are consumed for domestic heating, smithing and the manufacture of by-product coke. There is much competition from Pennsylvania and West Viriginia. In 1929 the production was 2,368,000 tons.

(18) *Washington.*—The coal districts are generally west of the Cascade Mountains. The mines are on the foothills of the slope and reach out to Puget Sound in the central and northern sections. The amount of alteration a coal has undergone seems to be roughly proportional to its distance from the Cascade Mountains. The sub-bituminous coals of Bucoda, Tono, Mendota, and Castle Rock, occur in a region of low relief, in which the Eocene coal has been but slightly disturbed. The railways absorb the largest output of coal, and next the domestic consumers, public utilities and cement mills. In 1929 the production was 2,252,000 tons.

(19) *New Mexico* coal is of Cretaceous age, and situated in Colfax, McKinley, Rio Arriba, Sandobal, San Juan, San Miguel, Santa Fe, and Socorro Counties. In 1929 the production was 2,340,000 tons.

(20) *Texas* coal is bituminous and lignitic, and is situated as follows: The bituminous coal is mined in Medina and Robertson Counties, while the lignite is taken from Houston, Milaru and Wood Counties. The lignites will not stand handling and are briquetted. In 1929 the production was 983,000 tons.

In comparing American with European coal-mining conditions and outputs, it should always be borne in mind that generally speaking American Carboniferous coal seams are much thicker and nearer the surface than the corresponding seams in Great Britain and Western Europe.

THE CHEMICAL COMPOSITION AND CONSTITUTION OF COAL.

From what is known of their origin and mode of formation it may be anticipated that all coals, whatever their geological age, will contain (1) various combustible organic compounds, complex in structure and of high molecular weight, representing the degradation or transformation products of the vegetable debris from which they were derived; and (2) variable amounts of mineral matter, which give rise to the ash remaining when the coal is burnt, and which represent partly the small amount of mineral matter in the original vegetation or the soil in which it grew, and partly also other associated mineral matters either deposited contemporaneously with the coal-field or subsequently introduced by infiltration.

The various organic bodies which together form what is sometimes termed the "coal-substance" all consist chiefly of the elements carbon, hydrogen, oxygen, nitrogen and sulphur, the relative proportions of which may be determined with considerable accuracy by the usual methods employed for the analysis of organic compounds. But the ascertainment of the nature of the various complexes which make up the coal-substance, and still more so of the relative proportions in which they are present in any particular coal, is a problem beset with difficulties.

Coal, when freshly mined, often contains much water ("pit water") and some occluded gas. Most of the water is lost on air-drying, the moisture-content of the air-dried coal depending on the nature of the coal itself and also on the hygrometric state of the atmosphere. The remainder of the water is completely lost when the finely divided coal is maintained for a short time at 105°C. The occluded gas may be withdrawn by continuous exhaustion of the finely divided coal either at the ordinary temperature or at 100°C. From a Durham coal, P. Bedson obtained 1·6 c.c. of gas per g., having a composition: CO_2 4·35, C_2H_6 6·65, CH_4 71·15, O_2 2·80, N_2 15·05%. From a Lancashire coal (Lower Mountain Mine), R. V. Wheeler obtained 1·375 c.c. of gas per g., containing NH_3 0·5, H_2S 0·5, C_2H_4 0·4, CO 2·1, C_2H_6 8·10, CH_4 80·35, O_2 0·4 and N_2 7·65%. More recently, F. Fischer, K. Peters and A. Warnecke (Brennstoff-Chem. 1932, **13**, 209) have drawn attention to the fact that the nitrogen contained in the gas from blowers and fire-damp may contain twice as much helium as is contained in atmospheric nitrogen. They suggest that such helium has a "fossil" origin and that the helium content of the gases may provide a means of determining the absolute age of coal.

The mineral matter in coal varies greatly in amount, composition and fusibility. It occurs in two distinct forms, one finely divided and more or less uniformly distributed through the coal substance ("inherent" or "intrinsic" mineral matter), the other segregated in bands or lumps ("extrinsic" mineral matter) and usually consists of shale (sp.gr. 2·5), together with some pyrites (sp.gr. 5·0), gypsum (sp.gr. 2·3), calcite (sp.gr. 2·7) and siderite (sp.gr. 3·8). If unduly great in amount, easily fusible, or highly pyritic, the mineral matter may affect detrimentally the commercial value of the coal. The intrinsic mineral matter originated in the inorganic salts essential to plant life which formed part of the parent vegetation, in salts concentrated by absorption and adsorption in the plant substance, and in dust brought down by wind and rain. Such mineral matter, by reason of its fine state of division and its intimate association with the coal substance, is not reducible in amount by the ordinary methods of cleaning. The extrinsic mineral matter (dirt) represents either sedimentary matter which was deposited contemporaneously with the coal-field, and which forms partings between the various seams, or mineral salts (*e.g.* pyrites, FeS_2, gypsum, $CaSO_4,2H_2O$, carbonates of lime, iron and magnesia) which may have been introduced by infiltration of various solutions after the vegetable matter was laid down. Such dirt is capable of being removed (to some extent) by hand picking or by mechanical cleaning.

The ash which remains when coal is burned is generally less in quantity and is qualitatively different from the mineral matter from which it is derived. Hydrated constituents such as shale and gypsum lose water, carbonates are decomposed, sulphide of iron is converted more or less completely into ferric oxide, while interactions may occur between the inorganic materials and the coal substance, resulting for example in the fixation of part of the organic sulphur in the residue. The limits of composition which may be expected in the ash from British coals are approximately: SiO_2 25–50, Al_2O_3 20–40, Fe_2O_3 0–30, CaO 1–10, MgO 0·5–5·0, TiO_2 0–3·0, alkalies 1–6, SO_3 1–11%. A fusible ferruginous ash is a constant and prolific source of clinkering troubles in furnaces and gas-producers. The melting-point of coal ash may vary between 1,000 and 1,500°C. (or even higher) according to its chemical composition and the conditions of heating; generally the melting-point is sensibly higher in an oxidising than in a reducing atmosphere, and usually rises as the relative *molecular* proportions of basic oxide to silica diminishes.

For purposes of comparison and classification of coals it is usual to disregard the variable proportions of mineral matter as well as of mechanically held water which they may contain, and to fix attention upon the character of the "coal-substance" itself. The coal substance, although always containing the same elements, carbon, hydrogen, nitrogen, sulphur and oxygen, is in reality a very complex material the constitution of which is only partly determined. The ultimate analysis of a coal consists in determining the percentages of elementary carbon, hydrogen, nitrogen and sulphur in a suitably prepared dry sample; the difference between the sum of these percentages *plus* the percentage of ash and 100 is usually returned as oxygen, apart from that in the associated mineral matter. The oxygen figure so deduced is, therefore, subject to whatever balance of error there may be in the total of the estimation of the other constituents, and, especially if the percentage of ash differs materially from the original mineral content of the coal, this error may be appreciable. Determination of carbon and hydrogen is carried out by combustion of from 0·2 to 0·3 g. of dried coal in an atmosphere of oxygen in a hard glass or silica tube, the products being passed over moderately heated lead chromate, which retains oxides of sulphur, and then over a heated silver spiral, after which the water and carbon dioxide are absorbed in dehydrated calcium chloride and soda-lime respectively.

Nitrogen is always present in coal, generally to the extent of between 1 and 2%. It is an important constituent, since it is the source of the ammonia obtained when the coal is carbonised. While, doubtless, the bulk of the nitrogen originates from the protein matter present in the parent vegetable matter, it has been suggested by H. Strache, H. Zikes and G. Polcich (Brennstoff-Chem. 1923, **4**, 244, 245) that part may result from the fixation by nitrogen-fixing bacteria of nitrogen adsorbed by colloidal humic acid. C. W. Shacklock and T. Drakeley (J.S.C.I. 1927, **46**, 478T) have shown that part of the nitrogenous constituents in coal is extractable by dilute sulphuric acid, the relative proportion so extracted decreasing with increasing maturity of the fuel. The nitrogen compounds in the extracts were identified as amides, diamino- and mono-amino acids. Determination of nitrogen is usually carried out by the well-known Kjeldahl process.

Sulphur is a highly undesirable constituent whether coal is to be burned in the raw state, carbonised or completely gasified. It is present chiefly in three forms, namely, as iron pyrites, sulphate of calcium (generally gypsum) and in organic combination. The sulphate sulphur is generally present to the extent of under 0·1%, though it may rise to 1% or over in weathered coals, and for this reason it is of less moment than either the sulphide or the organic sulphur. Although the sulphur is partly expelled (chiefly as H_2S, CS_2 and thiophen) on carbonisation, the greater part is usually retained in the coke. Sulphur is usually determined by the Eschka process, in which the finely-ground coal is intimately mixed with magnesium oxide and sodium carbonate and incinerated; the sulphur compounds in the solid residue are converted into sulphates by oxidation with bromine water, and the extracted sulphates are determined in the usual manner as $BaSO_4$ (*v.* Vol. II, 603*b*).

Researches on the constitution of coal have followed two main lines of attack: (*a*) microscopic, from the point of view of its palæobotany and petrology; and (*b*) chemical, by studying (i) the thermal decomposition of the coal substance, (ii) its extraction with solvents, and (iii) its degradation by controlled attack by chemical reagents followed by examination of the products. While some progress has been made, it must be confessed that less is known of the chemical nature of coal than of almost any important natural raw material.

(*a*) *Microscopic Examination.*—Bituminous coals are usually composed of more or less pronounced "bright" and "dull" bands or layers, while between them there is an amorphous powdery substance which is known as "mineral charcoal," "mother of coal" or sometimes "dant," the French name for which is "fusain." In 1919 M. C. Stopes (Proc. Roy. Soc. 1919, B, **90**, 470) designated four visible ingredients of banded bituminous coal, namely, *vitrain*, *clairain*, *durain* and *fusain*. The first two comprise *bright coal*, the third *dull coal*, and the fourth the *mineral charcoal*. *Vitrain* was described as being " a coherent and uniform whole, brilliantly glossy, indeed, vitreous in its structure " ; *clairain* as having " a definite and smooth surface when broken at right angles to the bedding plane, and these faces have a pronounced gloss or shine " ; *durain* as being " hard, with a close, firm texture, which appears rather granular to the naked eye " ; and *fusain* as occurring " chiefly as patches and wedges " and consisting of " powdery, readily detachable, somewhat fibrous strands."

In a later paper (Fuel, 1935, **14**, 4), Stopes has produced a comprehensive scheme of classification of coal ingredients in which the lithological types (vitrain, fusain, clairain and durain) are correlated with the petrological units of which they are composed.

Various suggestions have been put forward as to the origin of the bands in bituminous coal. Thus, D. White (Econ. Geol. 1933, **28**, 556) supposes that vitrain was formed from woody tissues deposited in stagnant water rendered low in oxygen-content and toxic to aerobic microbial action by the concentration of products of decay; much of the readily decomposable plant matter would so escape destruction and be preserved. Clairain would be formed under less protected conditions which still caused some retardation of decay. Further initial decomposition with consequent concentration of the more resistant plant remains, as well as the possible accumulation of fine drifted material would yield durain. Fusain is considered to have been formed by change of water-level with exposure of already humified material, which suffered partial decomposition leaving lignified cell walls cemented by a " humic paste." When carpeting successive laminæ in large numbers, fusain probably records seasonal exposure. G. Hickling (Presidential Address, Brit. Assoc. Sect. C, 1935) points out that each separate band or lenticle of vitrain may be regarded as representing a single fragment of wood, bark or other plant tissue, since improvement in microscopic technique has shown that the " uniform brown substance," formerly regarded as structureless and typical of vitrain, has generally been resolved into recognisable plant structures. Clairain consists of similar plant fragments which are individually too small to be distinguished without the microscope, mixed with more minute plant debris such as spores, isolated cuticles and other matter. He points out that fusain is usually woody tissue, clearly identical originally with much of that which has been converted into the uniform brown substance (the " vitrinite " of Stopes), but devoid of any organic substance in its cell cavities, and on account of its porous nature, often the receptacle for much of the mineral matter which has been deposited in the coal from solution, and consequently a high carrier of ash. Chemically, it is usually low in its content of hydrogen and oxygen and correspondingly high in carbon. Durain consists of a matrix of minutely macerated fragments containing a proportion of very finely fragmented " residuum " (the " micronite " of Stopes) which cannot be resolved under the microscope. Set in this matrix there are often seen large numbers of cuticles, spores (mega- and micro-spores), fragments of cuticle and sometimes resinous patches. The spores and cuticles are relatively unaffected by chemical attack and hence have been described by R. V. Wheeler as " resistant plant remains." So resistant are the spores, that A. Raistrick (Trans. Inst. Min. Eng. 1933, **85**, 225; *ibid.* 1934, **88**, 142) has shown that the microspores may be separated from the coal substance and the assemblage of types from any seam may be employed as a means of correlating occurrences of the seam which, by reason of faulting, folding or extensive " wash-outs " cannot be continuously followed over a considerable area.

(*b*) (i) *Thermal Decomposition of the Coal-Substance.*—The gradual thermal decomposition of the coal-substance at temperatures up to 1,000°C. or thereabouts has been studied by various investigators; but although much information of immediate value to the technologist has resulted, the method is too brutal for chemists primarily concerned with constitutional problems. Yet something may be learned from its results, especially those from immature brown coals, for although the temperature at which oils first appear is higher than that at which gas evolution commences, it is usually possible to distinguish *three* successive and independent effects of heat involving the expulsion (1) of carbon dioxide (*plus* some monoxide) and steam, as if by some internal " condensation," without any breakdown of the essential molecular structure; (2) of methane and other hydrocarbons, as if by the elimination of aliphatic side-chains from the coal complex (oils also appearing); and lastly (3) of hydrogen and carbon monoxide. And although such effects indicate three successive and independent changes, they more or less overlap and occur simultaneously over a considerable range of temperature.

" *Oil Point.*"—There is usually a definite temperature, situated between 250° and 375°C. at atmospheric pressure, but varying with different coals below which temperature the reaction is substantially the expulsion of steam and oxides of carbon (chiefly the dioxide) from the main organic substance. Then comes a temperature, fairly definite in each particular case, at which oil first appears. Whether the oil so appearing is merely " liquated " from the coal substance under the influence of heat, or should be regarded as a product of its decomposition, is perhaps a moot point, upon which the evidence though favouring " liquation " is not yet conclusive.

In cases of certain typical brown coals investigated at the Imperial College research laboratories (Bone and Himus, " Coal, its Constitution and Uses," p. 142) the results shown in Table IX were obtained.

In Table X are shown the amounts (in c.c.) of each of the several gaseous products evolved from 100 g. of the dry coal substance (i) up to the " oil point," and (ii) over selected temperature ranges thereafter, in experiments with the Morwell brown coal.

TABLE IX.—INITIAL DECOMPOSITION OF BROWN COALS AND LIGNITES.

Coal.	Oil point °C.	Weights evolved per 100 g. of dry dewaxed coal-substance.		Percentage CO_2 in gas evolved.	Mol. ratio H_2O/CO_2 expelled.
		Gas.	Steam.		
Morwell brown coal . . .	375	6·7	5·5	90·0	2·25
German brown coals:					
Rhenish .	260	4·9	5·0	93·2	2·6
	300	6·1	4·0	91·4	1·7
Saxon . .	288	4·6	3·5	90·9	2·0
	275	3·9	3·8	92·9	2·5
Saskatchewan brown lignites	320–360	4·5	4·5	70–75	—

TABLE X.—GASES EVOLVED FROM MORWELL COAL IN C.C. AT N.T.P. PER 100 G. DRY COAL SUBSTANCE.

Temp. range °C.	H_2S.	CO_2.	CO.	C_nH_m.	CH_4 and C_nH_{2n+2}.	H_2.
Up to 375	56	3,200	153	42	—	—
375–500	149	4,585	1,422	70	1,674	—
500–700	101	510	2,215	376	2,696	2,110
700–850	56	2,315	2,580	—	1,010	6,050
Totals	362	10,610	6,370	488	5,380	8,160

	To 375°C.	375–500°C.	500–700°C.	700–850°C.
Grams oxygen evolved as:				
CO_2+CO .	4·83	7·62	2·35	5·10
H_2O . . .	4·87	1·98	1·23	1·34

It should be noted that of the four principal gaseous products (CO_2, CO, CH_4 and H_2) in each temperature range (i) the carbon dioxide (accompanied by some CO and much H_2O) was the chief gaseous product below and much beyond the oil point (375°C.), and that from three-quarters to six-sevenths, respectively, of it had been evolved below 500°; (ii) next appeared methane, which was most freely evolved between 400° and 700°C.; and (iii) comparatively speaking, hydrogen was a late comer, being most freely evolved, together with carbon monoxide above 700°C. The thermal decomposition had practically been completed by the end of the experiment, during which almost all the oxygen in the coal had been expelled as steam and oxides of carbon.

With increasing maturity of the coal-substance, not only do the three successive effects of heat already referred to overlap more and more, but, because of the first stage (i) above becoming less important both relatively and progressively, with diminishing oxygen-content they become almost indistinguishable with well-matured bituminous coals.

Burgess and Wheeler (J.C.S. 1910–13) working chiefly with a South Yorkshire (Altofts) Silkstone coal, established 350°C. as the initial temperature of thermal decomposition of the main coal substance, a point which was marked by an abrupt and rapid increase in the evolution of gases. Up to such temperature only small quantities of occluded gases were evolved, although water began to be eliminated at 200°C., sulphuretted hydrogen at 270°, and oils at 310°. The last-named were considered as having been merely liquated out of the coal conglomerate. They also proceeded to study in detail (i) the rate of gas evolution, (ii) the total volume of gas and its composition, (iii) the amount of tar yielded by the coal at various temperatures between 450° and 1,100°C. It was found that (i) the evolution of methane and other paraffin hydrocarbons, which had been vigorous above 350°, almost ceased at 700°; (ii) that there was a well-defined "critical temperature" at about 700°C. marked by an abrupt and rapid increase in the evolution of hydrogen; and that (iii) the evolution of carbon monoxide more or less followed that of hydrogen throughout. Similar results were obtained with a South Wales (Abertillery) coal. Similar results have been recorded by other investigators both in France and the United States.

In a later paper R. V. Wheeler (Chem. and Ind. 1931, **50**, 345) took the following view of the course of distillation of a typical bituminous coal, the "decomposition point" of which he found to increase with its carbon content from 290° up to 365°.

"The course of the distillation of a typical coal is as follows: Over a range of temperature, beginning at about 220°C., and completed at about 300°C., there is a simple distillation of the hydrocarbon oils already present in the coal. These oils correspond closely in nature and quantity with those obtained by extraction of the coal. At a temperature of, say, 300° (which varies from coal to coal) there is a well-defined decomposition point of the coal substance, marked by the formation of much gas, water and oils. This decomposition completes itself over a narrow range of temperature. As the temperature is further raised to 320–330°C. the resins present in the coal distil in the water and oil vapour which is being simultaneously evolved, giving ether-soluble material very little changed from that present in and extractable from the coal. The resistant plant skins present in the coal are decomposed over the range 300–320°, giving rise to a comparatively large yield of tar, mainly of unsaturated hydrocarbon type, similar to that which can be obtained by distillation of modern plant skins. The yield of this portion of the tar naturally depends on the proportion of such skins, mainly spore exines in the coal, and is small with a bright clarain, and large with a durain."

"The most interesting feature disclosed by distillation is the well-defined and narrow range of true chemical decomposition, as distinguished from mere distillation of volatile matter already present. The decomposition point coincides with a marked change in the nature of the coal residue, which is evidenced, for example, in a marked enhancement of its oxidisability and reactivity in general, and in an increased response to the solvent or dispersing action of pyridine.

These properties suggest that the decomposition is of the ulmin portion of the coal, and this is confirmed by examination of the products of decomposition which contain much water and phenolic substances, known to be characteristic products of distillation of the ulmins."

The decomposition of the nitrogenous constituents of coal, formerly the source of most of the world's supplies of ammonia, was studied by O. Simmersbach (Stahl u. Eisen. 1914, **34**, 1153, 1200) who found that the nitrogen was distributed among the products of carbonisation as shown in Table XI.

TABLE XI.—DISTRIBUTION OF NITROGEN IN THE PRODUCTS OF CARBONISATION OF A SILESIAN COAL CONTAINING N 1·396%.

Carbonisation temperature °C.	Percentage of the Nitrogen appearing in				
	Coke	Gas.	NH_3.	Tar.	HCN.
600	71·69	18·13	7·81	2·12	0·25
700	65·43	12·13	18·13	3·65	0·66
800	63·65	10·73	21·28	3·47	0·87
900	58·40	12·14	24·12	4·15	1·19
1,000	49·98	21·53	23·15	4·11	1·23
1,100	41·39	30·51	23·09	3·70	1·31
1,200	26·43	45·10	22·84	4·21	1·42

It will thus be seen that while the maximum formation of ammonia occurs at 900°, upwards of 50% of the nitrogen remains in the coke up to 1,000° and more than 25% at 1,200°, and so firmly is the residual nitrogen contained in the coke that, according to M. G. Christie's researches (Inaug. Diss. Aachen. 1908), it is only very slowly expelled (as free nitrogen) as the temperature is gradually raised to 1,900°C., and he considers it to be present in the original coal in an extraordinarily stable " nitride " form as distinguished from the much less stable " imino " nitrogen, existing in organic compounds which decompose below 900°C. yielding ammonia.

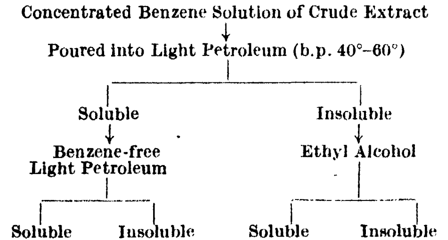
A certain amount of study has been devoted to the thermal decomposition of the sulphur compounds in coal, thus, Burgess and Wheeler found, with a Silkstone coal, that the evolution of H_2S began at 270° and virtually ceased at 300°C.; and there is much evidence of its not being evolved beyond 500° or thereabouts. On the contrary, thiophen and carbon disulphide are essentially high-temperature products. In an extensive investigation carried out at the Imperial College on the thermal decomposition of a brown coal from South Australia containing 3·7% of organic sulphur, the results shown in Table XII were obtained. On carbonisation, the organic sulphur constituents began decomposing with a disgusting odour at about 220°C., yielding thereafter increasing quantities of hydrogen sulphide, mercaptans and thio-ethers up to about 500°C., when their decomposition practically ceased with nearly 50% of the original sulphur still remaining in the solid residue.

TABLE XII. — PERCENTAGE DISTRIBUTION AMONG THE CARBONISATION PRODUCTS OF THE SULPHUR OF A SOUTH AUSTRALIAN BROWN COAL.

Temperature °C.	322	400	500	600	700
Percentage of the sulphur appearing :					
As H_2S . . .	8·1	11·3	17·4	18·5	18·9
As mercaptans, etc. . . .	11·9	30·0	30·3	30·3	30·4
In tar . . .	1·1	2·75	3·6	3·8	3·9
In residue . .	78·9	55·95	48·7	47·4	46·8
Percentage volatiles expelled . . .	15·5	32·3	41·4	45·2	46·6

(*b*) (ii) ***Extraction of Coal with Solvents.***—Since the publication in 1862 of the results of the pioneering work of de Marsilly, the application of solvents with a view to resolving the coal complex into identifiable constituents, has formed a popular method of attack; almost all the common organic solvents, either alone or mixed, have been tried; save, however, for the preliminary removal of resins, waxes, etc., which may be carried out by such solvents as benzene, alcohol, benzene—alcohol mixtures, ether or chloroform, the commonest solvents are pyridine, or benzene boiling under pressures up to 700 lb. per sq. in.

In broad outline, the procedure adopted by R. V. Wheeler and his associates (who have been its chief exponents) for the extraction of coal by pyridine, has been to effect a preliminary separation by this solvent, followed by division of the extracted material by treatment in chloroform into two further fractions, whereby the coal is resolved into (i) an *alpha* fraction, insoluble in pyridine, consisting of undispersed ulmins *plus* resistant plant remains; (ii) a ***beta*** fraction, soluble in pyridine but insoluble in chloroform, consisting of dispersed ulmins; and (iii) a *gamma* fraction, soluble in both pyridine and chloroform, consisting mainly of resins and hydrocarbons. C. Cockram and R. V. Wheeler investigated the *gamma* fraction from the clairain of Parkgate (bituminous) coal, extracting it successively with light petroleum, ethyl ether and acetone, styling the successive fractions γ_1, γ_2, γ_3 and γ_4 which they described as follows: γ_1 (about one-third of the total fraction) was of vaseline-like consistency, reddish-brown in colour and was found to consist of (*a*) saturated hydrocarbons, 40%, C 87·40, H 11·13%; (*b*) unsaturated hydrocarbons, 40%, no analysis given; (*c*) resins, dark red in colour, 20%, C 84·21, H 7·31%; γ_2 (about 37% of the total fraction) was a brick-red powder, m.p. 100–110°C., consisting mainly of resins and resin-degradation products (resinols, resines and resenes); γ_3 and γ_4 (12 and 18% of the total fraction respectively), consisted of a "resin-like" dark-brown powder, m.p. 280–300°C. without decomposition. They also consider that " insofar as the presence of a ' coking principle ' is necessary . . . the agglutinating medium during coke-formation consists of the resins and hydrocarbons formed during the early stages of heating in the coke-oven." Other investigators have also connected the coking propensities of coals with their content of the γ-fraction, while some have suggested that under carbonising conditions the β-fraction may assist. It is, however, generally agreed that the α-fraction, *i.e.* the insoluble residue of a pyridine-extracted coal, is quite devoid of coking propensities. Researches by Bone and co-workers have shown that in order to obtain reliable results, it is absolutely essential that the pyridine be pure and anhydrous and that, during the extraction process, free oxygen be totally excluded from the extraction apparatus. Various general observations have also shown that, besides any ordinary solvent action which pyridine may have upon the resinic constituents, which is probably fairly rapid, it also at the same time slowly attacks and resolves into simpler molecular aggregates the complex structure of the coal as a whole. Vignon (Compt. rend. 1914, **158**, 1421) studied the solvent action of aniline (b.p. 180°C.) and quinoline (b.p. 238°C.) on coal, and reported that of quinoline to be nearly three times as great as that of pyridine and twice that of aniline at their respective boiling points, which again suggests some "unbuilding" of the coal substance. So far the only solvent-extraction process of much chemical value is the benzene–pressure extraction originally introduced by F. Fischer and W. Gluud, but improved later by W. A. Bone and collaborators. Fischer and Gluud extracted coals with benzene at temperatures and pressures (275° and 50 atms.) approximating to the critical values of the solvent; but, not using the Soxhlet principle, their process was never complete and subsequently they divided their extracts into two fractions only, namely, "*Œlbitumen*" soluble in light petroleum, and "*Festbitumen*" insoluble therein. Bone and his collaborators introduced the Soxhlet principle at 500 and 700 lb.per sq. in. (which enables the extraction to be carried to completion), and subsequently resolved the crude extract into *four* fractions, as follows:


Concentrated Benzene Solution of Crude Extract
Poured into Light Petroleum (b.p. 40°–60°)
Soluble
Insoluble
Benzene-free Light Petroleum
Ethyl Alcohol
Soluble Fraction I
Insoluble Fraction II
Soluble Fraction III
Insoluble Fraction IV

They gave greater precision to the method, and extended its application to the elucidation of such questions as the nature, origin and development of the constituents of bituminous coals responsible for their coking propensities. The four fractions resulting from bituminous coal are characterised as follows:

I. *A yellow-brown viscous and usually non-nitrogenous neutral oil* of vaseline-like consistency, with C/H ratio usually <10 and low O content; soluble in light petroleum and apparently aliphatic in constitution. It may be divided into (*a*) and (*b*) according as it is volatile or not in steam.

II. *A reddish-brown amorphous solid, softening-point usually below* 60° with C/H ratio *circa* 13, soluble in a mixture of 1 part benzene and 4 parts light petroleum. (Fractions I and II are both combined in Fischer's "*Œlbitumen.*")

III. *A usually non-nitrogenous, reddish-brown solid with resinous lustre, softening usually below* 150°, with C/H ratio *circa* 12·5, insoluble in light petroleum (with or without benzene), but soluble in ethyl alcohol.

IV. *A neutral amorphous cinnamon-brown nitrogenous powder* insoluble in light petroleum or ethyl alcohol, softening usually between 150° and 250° with C/H ratio >15 and undoubtedly of a benzenoid character. (Fractions III and IV are combined in Fischer's "*Festbitumen.*")

The important feature of these fractions is that while I never (and II but seldom) has any "binding" properties, both III and IV always have, and that it is the two last (but especially IV) which chiefly determine the coking propensities of bituminous coals. The residue after the benzene–pressure extraction, which usually constitutes over 85% of the total coal substance, is always entirely devoid of coking propensities.

Semi-bituminous and anthracitic coals yield little or no benzene pressure extract. Sub-bituminous coals, lignites and brown coals, while always yielding Fractions I and II in proportions usually comparable with (and sometimes even greater than) those of bituminous coals, are either deficient in Fraction III and IV or do not yield them at all, in the latter case (*e.g.* brown coals, they yield instead of III, phenolic esters (III′), and instead of IV, phenolic and/or complex acidic bodies (IV′). Indeed there is already strong presumptive evidence that the constituents of bituminous coals chiefly responsible for their coking propensities originated in the phenolic bodies found in the less mature brown coals. Table XIII summaries the yields

TABLE XIII.—YIELDS OF BENZENE-PRESSURE EXTRACT.

Coal.	Yield of fraction.				Total yield.	C/H ratio in dry residue.
	I.	II.	III.	IV.		
Brown Coal:						
Morwell Brown Coal . .	3·5	1·5	1·0[1]	9·0[1]	15·0	19·2
Saskatchewan Brown Lignite . . .	1·65	0·3	0·3[1]	2·25[1]	4·5	19·6
Lignitic Coals:						
Alberta Black Lignite . .	1·3	1·3	1·2	0·5	4·3	20·3
N. Zealand sub-bituminous (non-coking)	2·9	1·7	2·4	1·2	8·2	—
Bituminous Coals:						
Shafton (weakly coking) .	3·5	2·1	2·3	2·7	10·6	18·6
Barnsley (coking) . . .	2·2	0·6	0·4	5·1	8·3	—
Busty:						
Durham (strongly coking) . .	3·3	3·0	0·05	9·25	15·6	19·5

---

[1] Not true Fraction III or IV, but the phenolic bodies from which they have been developed in more mature coals.

of benzene–pressure extracts from the different classes of coals referred to.

It does not necessarily follow from the experimental evidence that the phenolic bodies extracted from such brown coals were present in the free state therein; on the contrary, they seem more likely to have been present in some loose molecular association with the main coal substance, though as yet this is unproven. There is, however, much presumptive evidence for the view that the agglutinating Fractions III and IV yielded by sub-bituminous and bituminous coals have originated in the phenolic bodies found in Fraction III′ and IV′ of brown coals. And if, as now seems probable, such agglutinants so arise, during the maturing of coals, it was to be expected that some "intermediate" types of coals would be found in which Fractions III, IV, III′ and IV′ co-exist.

An example of such an "intermediate" type of coal has recently been furnished by the black non-laminated (apparently well-matured) lignite from Nam Ma, Shan States, Burma (No. 10, Table IV), which gave on extraction 11·10% of total extract resolvable as in Table XIV, as follows:

TABLE XIV.—RESULTS OF BENZENE–PRESSURE EXTRACTION OF NAM MA (BURMESE) BLACK LIGNITE.

Fraction.	Referred to the Dry Ashless Coal Substance.					
	%.	C.	H.	N.	S.	O.
I (*a*) .	0·1	No analysis made.				
I (*b*) .	1·6	82·5	9·8	trace	0·45	7·25
II .	1·4	76·25	8·6	0·25	0·30	14·60
III .	0·15	77·3	8·75	0·95	0·7	12·3
IV .	0·45	77·5	8·3	0·5	0·75	12·95
III′ .	3·45	Saponifiable esters apparently phenolic.				
IV′. .	4·0	Alkali-soluble bodies of phenolic nature.				

Fractions I and II resembled both qualitatively and quantitatively those from other immature coals previously examined. The presence, however, of bodies akin to Fractions III and IV in the neutral extract from a coal which also gave phenols and phenolic esters (Fractions IV′ and III′) indicated an intermediate type of extract. The compositions of Fractions III and IV differed from what would have been expected from a coal of the degree of maturity disclosed by the extraction results. The carbon and (more particularly) hydrogen contents were higher, and the oxygen was lower, than would have been predicted; also the compositions of the two fractions approximated much more closely than usual. Judged in the light of previous results, the prototypes of Fractions III and IV derived from the least mature coals in which these fractions occurred might be expected to have compositions approximating to:

	C.	H.	O.
	per cent.		
Fraction III.	70–74	5–6	above 19
Fraction IV.	below 77	5–6	above 16

In addition, the Fraction III, having been prepared from a neutral extract which had been previously treated with alkali, was neutral and therefore chemically different from the corresponding fraction of an extract of a bituminous coal or matured lignite type.

Although this is the first clear example of such an "intermediate" type of coal among those so far investigated in the Imperial College Laboratories, similar instances have been indicated elsewhere. So that altogether the view that the agglutinating fractions of bituminous coals originated in the phenolic bodies extractable from brown coals may now be regarded as well established.

(*b*) (iii) *Chemical Degradation of the Coal Substance.*—It has long been known that carbon dioxide, oxalic and acetic acids are among the products of even comparatively mild oxidation of coal; thus as long ago as 1829, Gay-Lussac obtained oxalic acid by oxidation of coal with nitric acid. It was not, however, until about 1920 that any marked advance was made, when Fischer and his associates oxidised coal suspended in an alkaline medium by air under pressure, obtaining small yields of a number of acids which indicated that the benzene nucleus formed an important unit in the chemical structure of coals. Later, Francis and Wheeler (J.C.S. 1925, **127**, 2236), from the oxidation of "soluble coal ulmins" with hydrogen peroxide and dilute nitric acid, obtained oxalic, succinic and small amounts of picric, pyromellitic and (possibly) trimellitic acids. Bone, Horton and Ward (Proc. Roy. Soc. 1930, **127**, A, 480) and Bone, Parsons, Sapiro and Groocock (*ibid.* 1935, **148**, A, 492), continuing the work of Bone and Quarendon, studied the alkaline permanganate oxidation of the residues left after the benzene-pressure extractions of coals, achieving for the first time, complete oxidation of the coal substance to identifiable products. They also extended the work to determinations of the quantitative distribution of the carbon in the coal substance among the oxidation products. The products of the alkaline permanganate oxidation included, invariably, carbon dioxide, acetic and oxalic acids, occasionally succinic acid and, at one time or another, all the possible benzene carboxylic acids with the exception of benzoic acid. In general, throughout the peat → coal → anthracite series, the more matured the coal substance, the less readily it is oxidised. The results of the researches may be summed up as follows:

(1) The experiments have proved conclusively, not only the essentially benzenoid character of the main coal substance, but its progressive development throughout the lignin → peat → coal → anthracite series, as the summarised results in Table XV show.

(2) In general, the ratio between the benzenoid and oxalic acids produced increased with the maturity of the coals.

(3) Some small proportion of succinic acid resulted from the oxidations of peats and brown coals, but not from lignins, bituminous coals and anthracites. It may have arisen from the oxidation of resins associated with the peat or brown coal.

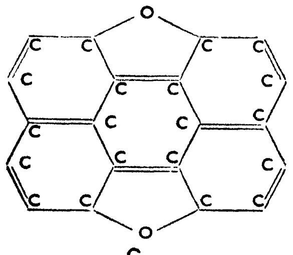
TABLE XV.—CARBON BALANCES: LIGNIN → ANTHRACITE SERIES.

Percentage of the carbon oxidised to	Lignin.	Peats.	Brown coals and lignites.	Bituminous coals.	Anthracite.
(1) CO_2 .	57–60	49–61	45–57	36–42	43
(2) Acetic acid .	2·5–6·0	3·0–5·5	3·0–7·5	1·5–4·5	2
(3) Oxalic acid .	21–21	15–28	9–23	13–14	7
(4) Benzene carboxylic acids .	12–16	10–25	22–34	39–46	50
Approx. ratios of (4) to (3)	0·5–0·75	0·64–0·9	1·5–2·0	3·0	7·0

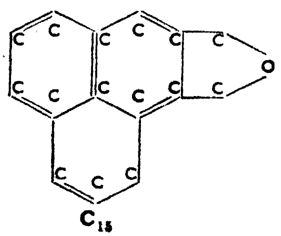
(4) While at one time or another every benzene carboxylic acid, except benzoic acid itself, has been isolated from the oxidation products, in every case so far examined the penta- or hexa-carboxylic acid has preponderated over the others. Only, however, with anthracite did the proportion of hexa- appear to exceed that of the penta-carboxylic acid in the products.

(5) While no phthalic acids were detected among the benzenoid acids produced from lignins, and comparatively small proportions among those produced from peats and brown coals, fair proportions thereof were found among those produced from bituminous coals and anthracites.

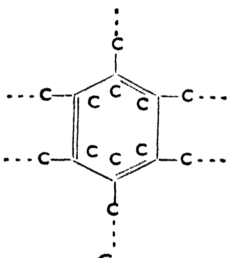
(6) The large proportion of both the benzene penta- and hexa-carboxylic acids among the oxidation products of coals indicates the preponderance in the coal substance of such benzenoid carbon complexes as:



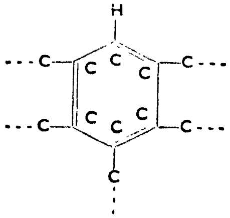
C_{20}



C_{15}



C_{12}



C_{11}

while the other acids might arise from simpler ring-structures with or without side-chains.

(7) While this suggests the possibility of the coal substance having arisen through condensations of phenolic- and amido-bodies with aldehydic bodies—much as synthetic resins are now produced—and there is evidence of at least the agglutinating constituents of bituminous coals having arisen in some such way—only further experiment can decide these questions.

(8) The results as a whole strongly support the view of the essential continuity of the lignin → peat → coal → anthracite series, and of lignins rather than celluloses being its chief progenitors. In this connection, however, E. Berl (private communication) has stated that on oxidising a "cellulose-coal" by means of alkaline permanganate, according to the Imperial College procedure (Bone *et al.*, Proc. Roy. Soc. 1930, **127**, A, 480; 1935, **148**, A, 492), he has succeeded in obtaining carbonic anhydride, oxalic, benzoic, phthalic, mellophanic, penta- and hexa-benzene carboxylic acids, as well as fatty (probably butyric) acids, and he regards such products as proving how easily carbohydrates may be transformed into aromatic substances, and therefore as still justifying his view of the cellulosic origin of bituminous coals. Seeing, however, that the conditions under which his artificial "cellulose coal" was produced—namely, by heating cellulose with alkaline solutions to 225–350° under pressure—differed considerably from those under which coals were naturally developed, it by no means follows that his experiments have any decisive significance in regard to the origin of bituminous coals.

As stated above, the benzenoid character of the main coal substance, whatever its origin, is now completely proved, although no constitutional formula for the "coal-unit" has been deduced as it has for the "cellulose" or "lignin" units.

That the coal substance contains unsaturated linkages is indicated by its behaviour on treatment with halogens. Experiments made at various times at the Imperial College (unpublished researches) have shown that when bromine acts upon a coal at room temperature or 100°C., both "addition" and "substitution," as well as some "adsorption," occur and that stable brominated products, outwardly resembling the original coal, result without any breakdown of its essential molecular structure. A. McCulloch and his collaborators (J.S.C.I. 1929, **58**, 167T; 1930, **59**, 377T; 1932, **61**. 49T, 186T; 1933, **62**, 47T) have found that coals may be vigorously chlorinated at air temperature, the first effect being "addition" at unsaturated linkages followed by "substitution," though not within the fundamental benzenoid nuclei. The coking propensities are simultaneously destroyed. The chlorine is said to be eliminated practically quantitatively when the chlorinated product is heated to about 500°C.

For a more complete account of the constitution of coal, *see* Bone and Himus, "Coal: Its Constitution and Uses" (1936).

THE VALUATION AND SELECTION OF COAL.

While the value of coal depends primarily upon its calorific value, other factors must be considered in determining its suitability for any given purpose, such as, for example, (i) moisture content, (ii) quantity, distribution and fusibility of the ash; (iii) the percentage of volatiles; (iv) the character of the carbonised residue; and (v) its ultimate composition—**C**, **H**, **S** and **N**—the **N** being important if the coal is to be carbonised or gasified in producers under ammonia-recovery conditions. Coal is not usually purchased in Great Britain on a basis either of calorific value or chemical analysis, but the practice is common in the United States and in certain European countries, the contract naming a definite price for coal of specified quality, subject to a sliding scale of bonus and of penalty for deviations from that quality. The following brief discussion is based on the appropriate specifications and reports of the British Standards Institute and "Fuel Testing," by G. W. Himus (L. Hill, London, 1932). In order that the results of the assay of a sample of coal may be of any value, it is necessary that the sample be representative of the whole bulk of the coal and shall contain the same proportions of large, medium and small, and in addition, the same proportions of clean coal and "dirt." Grumell and Dunningham (Report on the Sampling of Small Fuel up to 3 in. British Standards Institution No. 403, 1930) showed that sampling should be carried out by means of a number of equal increments uniformly distributed over the bulk of the coal, and furthermore that (*a*) the number of increments and/or the weight of sample, or the number of individual wagons to be sampled is independent of the weight of the consignment provided that the increments are uniformly distributed; and (*b*) the number of increments and/or the total weight of the sample, or the number of individual wagons to be sampled, must be varied according to the average error of the fuel (which is a function of the ash-content of the coal). Based on this and later work, methods of sampling coal and coke have been standardised by the British Standards Institution in a number of specifications (Nos. 404, 420, 496, 502). The tests most frequently applied to coal are those included under the title of "proximate analysis" (involving determination of moisture, volatile matter and ash), and determination of sulphur and calorific value. In certain special cases, other tests such as complete ultimate analysis, agglutinating value, tendency to swell when carbonised, the determination of phosphorus, or arsenic, or the fusion temperature and composition of the ash are sometimes required. For details as to the method of application of these tests, readers are referred to the relevant British Standard Specifications (*v. supra*, and also Nos. 453, 568, 686, 687 and 705) and to "Fuel Testing" (*op. cit.*).

With regard to the selection of coal for industrial purposes, while it is possible to indicate certain general rules which enable the observer to say that a particular coal will *probably* be suitable for a particular plant or purpose, plant and operating conditions are susceptible of such wide variation that the rules must be regarded only as broad generalisations. It can be stated quite definitely that unless it is required to produce a carbonised residue (semi-coke or coke), the use of strongly caking coal is to be avoided; furthermore, a high fusion temperature is desirable in the ash of coal which is to be burned in a furnace or gasified in a gas-producer. High moisture and high mineral content are always objectionable since both act as diluents, reduce the calorific value of the fuel and entail transport and handling charges. Generally speaking, uniformity of size is desirable, and it is always advantageous that successive deliveries of coal should be as far as possible of the same quality, since under modern industrial conditions uniformity of raw materials enables operating conditions to be standardised, a factor of great importance in maintaining high and steady efficiency coupled with low costs. Coal for the manufacture of gas generally yields from 30 to 38% of volatile matter (at 900°C. on the dry ashless coal) and a rather porous coke; the moisture and ash should be as low as possible. The best coking coals generally yield between 20 and 30% of volatiles and a strong, compact residue; the best steam coals yield from 8 to 20% of volatiles and should be non- or weakly-caking, the moisture and ash should be low, and the latter should be infusible to avoid formation of clinker; for gas–producer purposes, it is desirable that a coal should be non- or weakly-caking and have a low percentage of non-fusible ash, high volatiles are rather an advantage than otherwise; coals intended for low temperature carbonisation (at from 500 to 650°C.) should be low in moisture and ash and should give a non-swollen coke which is of sufficient strength to stand handling and transport.

STORAGE AND SPONTANEOUS IGNITION OF COAL.

It is well known that on storage coal deteriorates both as regards heating power and coking properties, a fact attributable to slow atmospheric oxidation, which may, under certain circumstances, give rise to spontaneous ignition of the coal. It was formerly believed that the oxidation of the iron pyrites present in coal is the principal cause of its spontaneous ignition, but it is now recognised that this is not so, the chief factor being the surface condensation of oxygen in the pores of the fuel, and subsequent oxidation of certain constituents of the coal substance. It has also been suggested, on the basis of experimental evidence, that in some cases of spontaneous combustion, the heat generated by bacterial acitivity is a factor to be considered. Coal readily absorbs oxygen when heated in contact with air at 150–200°, the process being not merely a physical absorption, but involving actual oxidation of coal substance; the weight first of all increases, and afterwards, especially if the temperature rises, steadily decreases owing to loss of moisture, to slow combustion and decomposition. According to investigations by S. W. Parr and others (Univ. of Illinois Bull. 1908, No. 17; 1911, No. 46), the oxidation of coal is continuous over a wide range of conditions, and begins with freshly mined coal at ordinary temperatures; at some temperatures between 200° and 275° (dependent upon the nature of the coal and the fineness of division) the oxidation becomes autogenous; actual ignition does not occur until the temperature rises beyond 350°. With regard to the influence of pyrites, it was found that the amount of " pyritic oxidation " under given conditions is always proportionate to the pyritic content of the coal, so that an increase in the latter may therefore hasten " the rise in temperature up to the critical point at which the absorption of O by the coal itself is rapid enough to increase the temperature up to the point of self-ignition." Hence, pyritic oxidation may become a contributory (though not the chief) factor in the spontaneous ignition of coal, although *by itself*, and apart from the simultaneous oxidation of the coal substance, it would be negligible. According to Parr and Cressman, the presence of moisture increases the reactivity of the coal–air system at any temperature. The whole phenomenon is probably one of " surface combustion." According to Bone (" Coal and Its Scientific Uses," 1918, p. 158) the absorption of O by typical British (Durham and Yorks.) bituminous coals is very slow at temperatures below 80°, and is attended by the production of relatively insignificant quantities of the oxides of carbon. But in the neighbourhood of 80° the action becomes much quicker, and at above 100° is marked by the regular and simultaneous production of both the oxides of carbon as well as of steam, all of which apparently result from the decomposition of some unstable " oxygenated " body primarily formed by the absorption of the oxygen. In 1923 M. C. Stopes and R. V. Wheeler (Fuel, 1923, 2, 29–41, 83–92, 122–127) published the results of experiments on British bituminous coal made by them at the Home Office Experimental Station, Eskmeals, from which they concluded (1) that whereas the occluded gases removed from freshly won coal on exhaustion at 100°C. consist mainly of paraffin hydrocarbons, they contain a large proportion of oxides of carbon if the coal has been previously " weathered " either naturally or artificially, as though oxygen had reacted with some part of the coal substance similarly to its reaction with pure carbon; (2) the greater part of the oxygen absorbed by the coal at temperatures between 15° and 100°C. ultimately appears as oxides of carbon (the ratios CO_2/CO varying between 3·8 and 12·7) when the coal is exhausted at 100°; and (3) that at such temperatures the chemical reaction following upon the physical absorption varies in degree, and perhaps also in nature, as between the various banded constituents of the coal. In 1925, S. W. Parr and R. T. Milner (Ind. Eng. Chem. 1925, **17**, 117) by further experiments in which representative Illinois bituminous coals were maintained for as many as 50 days under closely controlled conditions in currents of oxygen at various temperatures up to 110°C., found that (i) the coals increased in weight throughout each trial, approaching " saturation " after such increase amounted to about 8%, (ii) from 4 to 8% by weight of moisture and from 2 to 6% of carbon dioxide were evolved, the amounts increasing with the temperature, and (iii) the loss in calorific value at 100° was about 8% in 50 days, while at 150° it was as much as 25%. It was concluded that at atmospheric temperature oxygen is primarily absorbed with corresponding increase in weight, the calorific value decreasing *pari passu* with the gain in weight. At higher temperatures, however, the absorbed oxygen undoubtedly enters into chemical combination with the coal substance and is ultimately evolved chiefy as H_2O and CO_2, with consequent loss in potential energy. Although doubtless many points require further investigation, sufficient is now known to warrant the conclusion that, whatever subsidiary part (if any) pyrites may play, the main and predominating cause of the spontaneous combustion of coal residue is the coal substance itself, which is oxidised more or less readily according to its constitution. It is also evident that the oxygen is first of all adsorbed by the coal substance, possible in some " activated " form, then in some way more or less loosely incorporated with it, and as the temperature rises it is finally expelled in gaseous products, chiefly as H_2O and CO_2. But between its initial absorption and its final expulsion, a whole series of complex phenomena are probably involved which so far have received little attention and need elucidation. With regard to the storage of coal, it has has been proved that coal stored *under water* suffers no deterioration. The conditions most favourable to spontaneous ignition of coal when stored in heaps are (1) a certain, but not excessive, ventilation of the heap; (2) a certain degree of subdivision (*e.g.* small coal mixed with dust); and (3) any circumstance which tends to heat conservation in the heap. The best safeguard is either excessive ventilation (which it is practically impossible to maintain in large stores or in a ship's hold) or no ventilation at all. The extinction of fires which may break out on board ship is often a matter of great difficulty, the most effective method being that proposed by Harker (7th Int. Cong. Appl. Chem. 1910, *also* J.S.C.I.

1918, **34**, 157T) whereby the flue gases from the boilers of the vessel are pumped into the burning hold.

A. C. Dunningham and E. S. Grumell (J. Inst. Fuel, 1937, **10**, 170) have shown that effective protection against self-ignition of coal in large piles may be obtained by ventilation ducts on the windward sides only, provided the stacking is carefully carried out and the pile compacted by rolling. Furthermore, such ventilated piles of Derbyshire, North Staffs and Lancashire slacks, beans and pearls showed little if any deterioration in calorific value or in size after 3½ years' storage.

THE COMBUSTION OF COAL.

When bituminous coal is charged into a hot furnace, it first of all undergoes a process of destructive distillation; its least stable resinous constituents decompose, and hydrocarbons are freely evolved, which, on partial oxidation or secondary decomposition, give rise to carbon, together with minute quantities of dense tarry vapours (smoke) which are difficult to burn, except in an abundant air supply and at high temperatures. The residual coke fuel, being raised to incandescence, is burnt by the air, which is drawn in through the grate, to CO and CO_2 in the ratio of between 2 and 3/1. If, as in intermittent stoking, the furnace be cooled by a sudden inrush of cold air during the introduction of a fresh charge of fuel, smoke will be freely evolved. The production of smoke may be greatly reduced by the adoption of continuous mechanical stoking, especially if it be on the "under-feed" principle, or by making the mixture of "smoke" and *hot* air impinge upon an incandescent fireclay surface; the introduction of a pre-heated secondary air supply near or at the fire-bridge of the furnace will often diminish smoke. It is never possible to burn coal in a furnace with the theoretical quantity of air; thus, 1 lb. of coal containing C 80·0, H 5·5, S 0·9, N 1·5, O 5·0 and ash 7·0%, would, theoretically, require 136·0 cu. ft. of dry air at 15° and 760 mm. for complete combustion, and the cooled gaseous products would contain 18·2% CO_2. It rarely happens, however, that the CO_2 content in the cooled chimney gases from a coal-fired furnace exceeds 13·0%, and the more usual proportion is from 8·0 to 10·0%. In large boiler installations, the adoption of mechanical stoking, together with automatic instruments for recording the temperature and CO_2 content of the chimney gases, will be found conducive to fuel economy. E. J. Constam and P. Schläpfer of the Zürich Prüfungsanstalt für Brennstoff, as the result of exhaustive boiler trials with many different coals, concluded that those yielding between 16 and 23% of volatiles (referred to dry ashless fuel) have the greatest steam-raising values; with coals yielding a high percentage of volatiles, there is an excessive loss on account of their incomplete combustion. On the other hand, with a coal low in volatiles, and which, therefore, yields a large percentage of coke in the boiler furnace, a considerable excess of air must be used in order to maintain combustion at a rate sufficient to ensure rapid evaporation in the boiler, and this means an excessive loss as sensible heat of the chimney gases. In trials on a marine boiler with coals yielding between 16·5 and 19·1% volatiles, evaporating about 3·6 lb. of water per sq. ft. of heating surface per hour, between 73·7 and 75·1% of the heat of combustion of the fuel was transmitted to the water, about 20% was lost in the chimney gases (at 276–303°), partly as sensible heat and partly as unburnt gases, another 3–3·4% was lost in the ashes, the balance representing radiation losses (Z. Ver. deut. Ing. 1909, 1857). In trials on a goods locomotive on the Furness Railway, fired with Yorkshire, Lancashire, Cumberland, Scotch and Welsh coals, the average boiler efficiency reported was 74·5% for an average evaporation of 8·65 lb. of water per sq. ft. of heating surface (Pettigrew, J. Iron and Steel Inst. 1903, ii. 206).

The results of a large number of boiler trials, each lasting a full working day, were summarised by D. Brownlie ("Boiler Plant Testing," Chapman and Hall, 1922), in which he found that the true average net working efficiency (allowing for steam used as auxiliary to the operation of the boilers) was only 58%, varying from a maximum of 82·2 to a minimum of 32·5% for the whole plant, including economisers and superheaters (where fitted). The average net working efficiencies of cylindrical boiler plant (Lancashire and Cornish) was only 60%, while water-tube boiler plant showed an average of 69·2%. Although there has been some improvement during the past 15 years, there is still much progress to be made before the practical limits of boiler efficiency in general industrial practice will have been reached.

2. SECONDARY OR DERIVED FUELS.

(*a*) **From Wood.**—*Charcoal* (*v.* Vol. II, 310*c*).—Charcoal is an excellent fuel for metallurgical purposes on account of its low percentage of ash, its freedom from sulphur and phosphorus and its easy combustibility. A recent development in the use of charcoal has been in its application to the propulsion of road vehicles. The charcoal is gasified in small portable gas-producers and the gas thus formed is burned in the engine of the lorry or truck. Experiments on these lines have been made, *inter alia*, in South Africa (Fuel Research Inst., Bull. No. 5, 1936) with charcoal made from wood or mealie cobs, and it was found that, using a "Suedlund" producer fitted to a Chevrolet 30-cwt. lorry, from 12 to 14 lb. charcoal were equivalent to a gallon of petrol during a journey of 370 miles over poor roads at an average speed of about 20 miles per hour. In an article by Marshall Petain (L'Auto. 1936, No. 27) it is stated that 1 litre of liquid fuel is equivalent to 1·5 kg. of wood charcoal or 3 kg. of dry wood. It is stated also that the latest automobile consumption per km. per ton of total weight is from 120 to 150 g. wood, or 75 g. wood charcoal, giving operating costs about 50% lower than with liquid fuel. Comparative tests have also been made with two 1-ton Ford vans during the journey from London to Afghanistan, using local charcoals *en route*. The relative fuel costs for the 1,300-mile journey from London to Baghdad were stated to be £3 17*s.* 6*d.* with charcoal at £7 5*s.* per ton and £10 12*s.* 6*d.* with petrol (Engineering, 1934, **137**, 132).

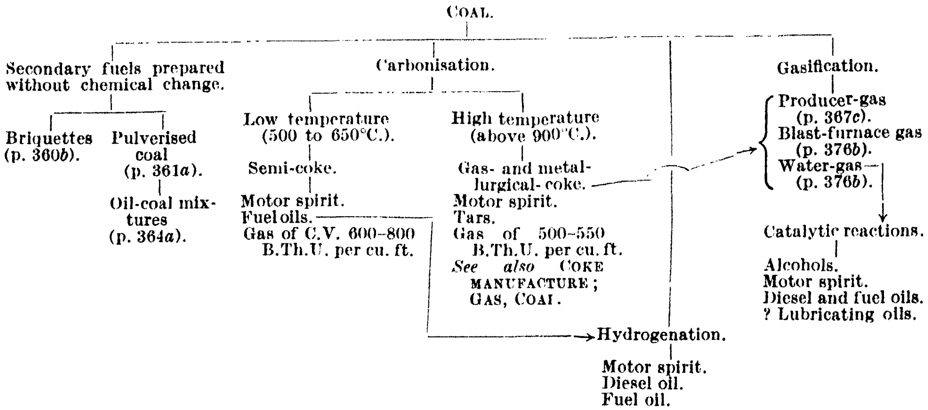
(*b*) **From Peat.**—*Peat charcoal* is very friable and porous, and consequently difficult to use in metallurgical operations. When sufficiently coherent, and when the percentage of P_2O_5 is low, it may be used in low, small furnaces. The carbonisation may be effected in open kilns, in pits or in ovens in which the air for combustion passes from above downwards, or by external firing in closed vessels, in order to enable the volatile products of distillation to be collected. Peat charcoal is easily kindled, and has a calorific power of 6,500–7,000 g.-cal. It is not adapted for smelting iron, but may be used advantageously for gas furnaces, on account of the large size of the lumps, absence of clinker and the fact that the ash readily falls through the bars.

Experimental work on the carbonisation of peat in vertical gas retorts is described in Technical Paper No. 4, of the Fuel Research Board (1921). The following yields were obtained per ton of peat containing about 20% of water:

Carbonising temperature °C.	980	850
Coke, cwt.	5·4	5·4
Tar, gallons	12·6	21·3
Ammonia liquor, gallons .	95·5	87·5
Ammonium sulphate, lb. .	29·2	24·8
Gas, cu. ft.	14,900	13,760
Calorific value of gas, B.Th.U. per cu. ft. at N.T.P.	348	364

(*c*) **From Coal.**—The relationship between coal and the fuels derived therefrom is illustrated diagrammatically in the annexed scheme. The quantity of coal used for the production of derived fuels (excluding that gasified in gas-producers) in Great Britain in 1935, amounted to 42 million tons or 18·9% of the total output, distributed as follows: briquetted, 0·9; pulverised, 5·1; carbonised, at gasworks, 18·0, at coke ovens, 17·4, at low temperature carbonisation plants, 0·3; and hydrogenated, 0·3 million tons.

DIAGRAM SHOWING THE RELATIONSHIP BETWEEN COAL AND THE FUELS DERIVED THEREFROM.


COAL.
Secondary fuels prepared without chemical change.
Briquettes (p. 360*b*).
Pulverised coal (p. 361*a*).
Oil-coal mixtures (p. 364*a*).
Carbonisation.
Low temperature (500 to 650°C.).
Semi-coke.
Motor spirit.
Fuel oils.
Gas of C.V. 600–800 B.Th.U. per cu. ft.
High temperature (above 900°C.).
Gas- and metallurgical- coke.
Motor spirit.
Tars.
Gas of 500–550 B.Th.U. per cu. ft.
See also COKE MANUFACTURE; GAS, COAL.
Hydrogenation.
Motor spirit.
Diesel oil.
Fuel oil.
Gasification.
Producer-gas (p. 367*c*).
Blast-furnace gas (p. 376*b*).
Water-gas (p. 376*b*).
Catalytic reactions.
Alcohols.
Motor spirit.
Diesel and fuel oils.
? Lubricating oils.

Briquettes (patent fuel).—The inevitable production of more or less fine coal (which is often difficult to dispose of commercially) during mining has led to the development of briquetting processes whereby the fine material is converted into solid and coherent cakes which are suitable for burning on grates, domestic or otherwise. The annual world production of briquettes is about 50 million metric tons, of which some 36 million (31 million from brown coal) are made in Germany. If the natural wax content of a brown coal is sufficient, it is possible to form briquettes without the addition of a "binder." The raw coal is crushed and then dried until the moisture-content is between 12 and 17%; it is essential that the raw material should enter the presses at from 30–40°C., therefore the dried material must be cooled to within this temperature-range. The next step consists in forcing the dried brown coal through an orifice by means of a reciprocating stamp whence it is extruded against a rope of previously pressed briquettes moving outwards. The compressed brown coal emerges from the press as a long bar of glossy black fuel which, on cooling, separates into single briquettes. Such a process of "dry" briquetting cannot, however, always be applied to brown coal, and never to bituminous coals and anthracites; it is then necessary to supply a binder from external sources. The most satisfactory binders are coal-tar, petroleum pitch or natural bitumen because they are readily combustible, do not add to the natural ash-content of the fuel and render the briquettes waterproof. A number of other binders such as maize meal, farina or potato starch (together with a small percentage of lime) or sulphite liquor are used where pitch is either unobtainable or too expensive; in warm dry climates such binders meet with some success, but the briquettes are not weatherproof. Inorganic binders such as clay, Portland cement, magnesia cement and lime have been used, but are open to the serious objection that the mineral-content of the briquettes is increased. Starch may sometimes be usefully employed as a substitute for part of the pitch (1 part of starch replaces about 2 parts of pitch), but there is a limit imposed to such replacement by the extent to which it is desired to produce waterproof briquettes. Experimental work has been carried out in the production of briquettes from bituminous coals by preheating them until they become plastic and then applying pressure, but this process has not yet reached the stage of commercial development.

When employing a binder, it should be broken up and fed, along with the dried coal into a mixer for accurately measuring out the proportions of the two materials, which then pass into a disintegrator, where they are ground together to the required degree of fineness. The ground mixture is then delivered to a vertical heater, where it is heated by means of superheated steam so as to render the binder plastic and adhesive. Thence it passes to the briquetting machine, where it is compressed into rectangular or ovoid briquettes. In the latter case, the material passes between two rollers on the perimeters of which are opposing ovoid cavities into which the coal/binder mixture is compressed at a maximum pressure of 2 tons per sq. in.

Pulverised Coal.—The speed and completeness with which a fuel can be burned are a function of the intimacy with which it can be mixed with the air necessary for combustion. In this respect, finely pulverised coal has the following advantages: (i) it may be intimately and uniformly mixed with the air required for combustion and burned completely with a minimum excess, leading to high furnace temperatures and low flue losses; (ii) it can be pumped through pipe-lines and handled with the same ease as a fluid; (iii) a furnace fired with pulverised coal is extremely flexible under rapid variation in the load, since the supply of coal can be varied almost instantaneously by operating a valve; (iv) the absence of a fuel bed eliminates troubles due to clinker formation, consequently the ash content of the coal is of relatively little moment so far as the combustion process is concerned; (v) the furnace atmosphere may be maintained either oxidising or reducing at will; this is of particular moment in metallurgical furnaces, since by maintaining a reducing atmosphere in contact with the charge, scaling losses are minimised.

The range of fuels suitable for pulverising is very great; provided the feed material to the pulveriser is sufficiently dry to be free-milling, fuels yielding up to 40% of ash can be burned in the pulverised condition with a loss of only 5% of combustible. While, however, such high ash materials can be successfully handled, it must be decided by circumstances whether it is an economic proposition to do so, bearing in mind that extra pulverising cost is entailed in fine-grinding the incombustible matter, while at the same time, additional wear and tear results lead to enhanced maintenance and repair charges.

The essential parts of a pulverised coal plant are means for preparing the coal, and a burner to deliver the fine product with the air necessary for combustion into the furnace. There are three general systems in operation, namely, the "central-grinding" which was first in the field, the "unit" or "direct-firing" and the "bin and feeder" system. In the earlier form of central-grinding plant, there was a central mill house in which the coal was roughly crushed, dried, pulverised and stored, and from which it was distributed as requisite to the individual furnaces. In the direct-firing system, each furnace with its combustion equipment forms a self-contained unit consisting of mill and burner. The pulveriser receives a regulated feed of raw or roughly crushed coal and delivers the fine product direct to the furnace through a suitable burner; no separate dryer is employed, but drying may be carried out in the mill when in operation by passing through it a current of hot air which forms the primary air supply to the burner. The advantages of the direct-firing system as compared with the older central-grinding system are its simplicity, low first cost and the small floor space required. On the other hand, the direct connection of the pulveriser with the burner, although it makes for simplicity, is not altogether a desirable feature, since the load on the mill varies with the requirements of the furnace, and in the event of a failure of the pulveriser, the whole unit must be shut down while repairs are carried out.

In the more modern bin and feeder system, therefore, while the intimate association of pulveriser and furnace characteristic of the direct-firing system is still maintained, the storage bin of the older central-grinding plant is retained and the transport plant is so arranged that the product from each mill may be delivered into any of the several storage bins. The pulverisers are thus able to operate at their designed and most economical outputs and in the event of the breakdown of any mill, the bin which it normally supplies may be fed from one of the other pulverisers.

Drying of the coal is necessary in order to prevent hanging up and arching in storage bins and to reduce the chances of spontaneous combustion. The capacity of a given mill is increased and the power consumption is diminished as the moisture content of the coal is reduced. During grinding, the temperature of the mill rises, moisture is driven out of the coal if not previously dried, and such moisture may be re-deposited in any parts of the system which may be inadequately insulated, leading to the formation of obstructions consisting of wet coal in the transporting lines. In direct-firing plant, preliminary drying is of less importance than in bin and feeder plant, since, owing to the short passage between the pulveriser and the furnace, the drop in temperature is negligible, consequently condensation does not take place; also the coal is aerated and agglomeration of particles is less likely. In modern bin and feeder plant, separate dryers are less frequently installed than formerly; drying is carried out in the mill by means of hot air or hot flue gases.

While from the point of view of combustion the finer the degree of grinding the better, a limit is imposed by the practical considerations that the power consumption increases with the fineness of the product and at the same time the capacity of the mill falls off. A compromise must, therefore, be adopted, so as to ensure such a degree of fineness that no particle of coal shall be sufficiently large that it will either fall out of the air stream or pass right across the furnace and escape unburned with the waste products.

The necessary degree of fineness depends on (*a*) the density of the coal, (*b*) the percentage of volatiles, and (*c*) above all, the combustion-volume available. The smaller the combustion chamber and the lower the volatile yield of the fuel, the finer and more uniform must be the grinding.

It is found for normal coals that good furnace conditions are obtained if the product shows the following screen analysis :

	%
Passing B.S. Sieve No. 44 . .	99
" " " 100 . .	85–88
" " " 200 . .	55–65

In bin and feeder, and central-grinding plant, means must be provided for transporting the pulverised coal, and there are two general methods in use, namely, by means of compressed air or mechanical transport. In the blowing-tank system, charges of coal are blown as required from air-tight containers, which may be mounted on weighbridges. The mixture of coal and air is received in cyclones where separation takes place, the coal being then delivered by gravity into the storage bins. In the Fuller-Kinyon pumping system, the pulverised coal is continuously fed into a pump which consists of a long steel or cast-iron screw, driven at a high speed in a cast-iron cylinder which discharges into a pipe-line through which the coal is transported. A small quantity of compressed air is injected into the coal near the point at which it leaves the screw and enters the pipe-line. The air prevents the coal from packing, thereby facilitating the action of the screw in forcing it through the delivery pipe. Pumping plant has an advantage over the other transport systems in which compressed air is used in that, owing to the limited amount of air which passes with the coal, no cyclones are required to effect separation of the coal and air ; capital cost and space are thereby saved, since the coal is delivered directly into the storage bins. This system has been used for delivering coal at distances up to 2,000 ft., and for lifts up to 100 ft. In the purely mechanical class is the screw-conveyor method of transport, in which the coal is transferred by screws working in suitable troughs. This method was first in the field, but had the disadvantages that it was not easily adaptable to changes of direction or to lifts except those involving very gentle slopes, consequently it has generally been superseded in later plant. The closer association of the pulverisers with the furnaces, which is the present tendency, has minimised these objections, and the mechanical transport system is likely to regain its former popularity.

The coal having been supplied to the furnace bin is passed by means of a feeder to the burners. The function of the feeder is to deliver the coal uniformly and without pulsation to the burner, which, in its turn, when supplied with a correctly proportioned mixture of coal and air, should deliver a uniform mixture into the furnace. While there are numerous makes of pulverised-coal feeder, the general principle underlying their design is the same, namely, that small, equal quantities of powder are picked up by a suitably divided wheel or fluted drum and thence dropped into the stream of primary air on its way to the furnace. Although several types of pulverised-coal burners are available, all modern burners employ low air-pressures and, in general, are designed to secure a thorough mixture of the coal with all the air required for combustion near its point of entrance to the furnace, while some, in addition, attempt to secure turbulence of gases in the furnace. The choice of a burner must be influenced profoundly by the furnace in which it is to be installed, depending on whether there is ample combustion space, and whether the furnace is provided with water-cooled or refractory walls.

The earlier pulverised-fuel furnaces were of conventional type, having solid refractory walls, but erosion difficulties arising from slagging of the ash were so serious that modern furnaces are generally provided with walls made up of tubes which are connected with the water spaces of the boiler. The tubes may be bare and so exposed to the full radiation of the furnace, they may be embedded in refractory bricks which are thus cooled and prevented from overheating, or alternatively, they may be covered on the fire side by refractory cast-iron blocks which are clamped to them. The bottom of the furnace is provided with a " water-screen " of widely spaced tubes also connected with the water system of the boiler ; the ash thus enters the ashpit *via* a cooling zone, and is delivered as solid particles and not as slag.

Instead of being water-cooled, one or more walls of the furnace may be cooled by passing the secondary air through suitable passages, thus simultaneously protecting the walls and pre-heating the secondary air.

In Fig. 2 (Bone and Himus, *op. cit.*), the arrangement of a modern boiler plant fired by pulverised coal is diagrammatically shown. It will be appreciated that in a water-walled furnace, such as is illustrated, the utmost advantage is taken of heat transfer by radiation, in fact, in certain modern plant, no less than 85% of the heating surface is exposed to radiant heat, only 15% of convection-heating surface being provided.

In the Combustion Steam Generator, the furnace is entirely surrounded with water-tubes and the burners are arranged at the corners of the furnace so as to deliver the coal—air mixture tangentially to an imaginary circle about 4 ft. in diameter, thus imparting a swirling motion to the contents of the furnace ; the result is that the gases are thoroughly mixed with consequent rapid and complete combustion. At the Congella Power Station, Durban, two such generators have been installed, each designed for a continuous evaporation of 120,000 lb. per hour and operating at 270 lb. per sq. in. with a guaranteed thermal efficiency (based on the net calorific value of the coal) of 90·5%.

The application of pulverised fuel to internally fired boilers (Lancashire and marine) has given rise to special problems by reason of the small furnace volume. Whereas in a water-tube boiler of any given capacity the furnace can be designed to suit the fuel and method of firing, in an internally fired boiler, short of fitting an external combustion chamber (which is usually impracticable owing to the extra space required), the furnace volume is rigidly limited by the size of the boiler, and attention has therefore been concentrated on improved burner design to secure rapid and complete combustion. For successful operation, uniform and fine grinding is necessary to ensure that no particles of coal fall out of suspension before combustion is complete. A number of plants consisting of batteries of Lancashire boilers are in successful operation and the use of pulverised coal for marine propulsion is making some headway.

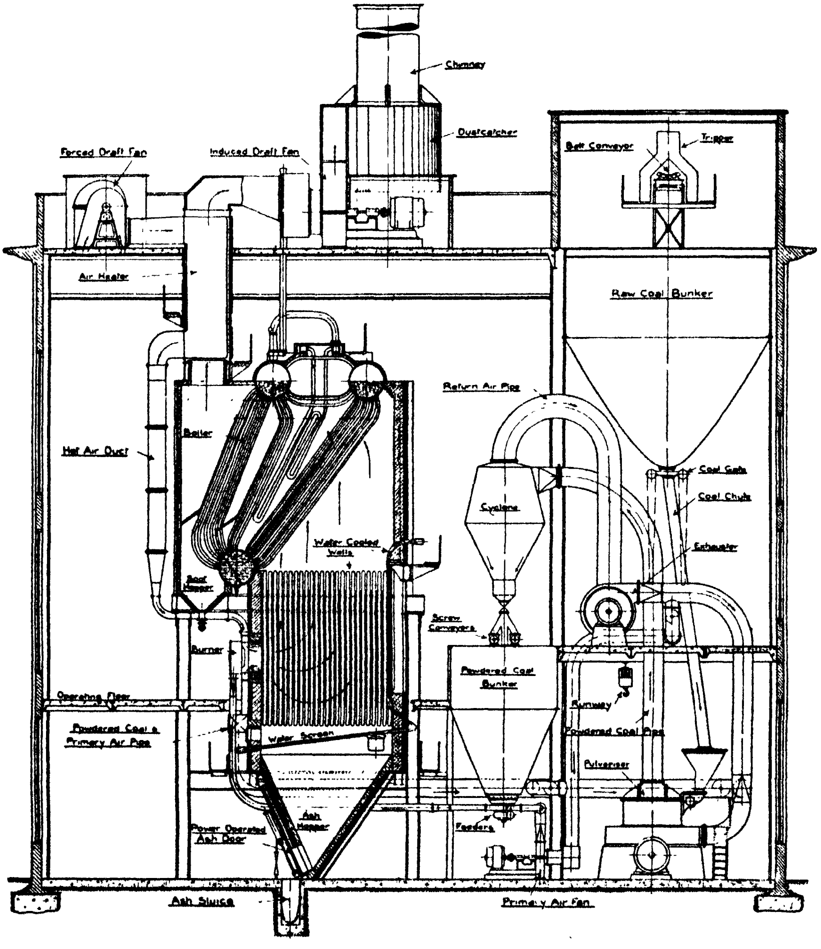


Fig. 2.—Diagrammatic Arrangement of Modern Boiler Plant Fired by Pulverised Coal.

An important development now in the stage of large-scale experiment is the use of a substantially de-ashed pulverised coal for power-production in internal combustion engines of the Diesel type, and already progress has been made in this direction in Germany and Austria. Pawlikowski, formerly associated with Diesel, maintains that to adapt a Diesel engine to pulverised coal, little alteration is necessary beyond the provision of a special admission valve and a pre-combustion chamber for the fuel, and that the only serious mechanical difficulty so far encountered has been due to leaking piston rings allowing the powdered fuel and ash to grind between the piston and cylinder lining; but such trouble is said to have been overcome by using linings made of special steel.

No valve trouble has been reported, the ash (it is said) being blown through the valves as an impalpable powder. This is a point on which judgment should be reserved. It would be advantageous to work with a pulverised coal of lowest possible ash-content, such as might be prepared by a de-ashing process; probably research on the explosive properties of such fuel will lead to improvement in engine design.

Oil—Coal Mixtures. "Colloidal Fuel."—Although potential heat in the form of coal is generally cheaper than in the form of oil, liquid fuels possess certain advantages, particularly for marine purposes, in that they are more readily handled and permit more economical utilisation of bunker space; the thermal storage capacity of a given bunker is, in fact, about 40% greater with oil than with coal.

A suspension, however, of finely powdered coal and oil is, by reason of the fact that the specific gravity of coal is 30–40% greater than that of fuel oil, the most compact fuel known; thus, for example, if a coal of sp.gr. 1·35 and calorific value 14,500 B.Th.U. per lb. be made into a 40/60 mixture with fuel oil of sp.gr. 0·90 and calorific value 19,000 B.Th.U. per lb., the mixture has a potential heat content of nearly 11·2 therms per cu. ft., as compared with 10·7 for oil or 7·2 for coal alone. Apart from the greater concentration of heat in coal—oil mixtures, other advantages are the absence of deterioration and self-heating to which many coals are liable. Coal—oil mixtures having specific gravities of about 1·04 can be stored under a water seal, thus reducing fire risks, while in the event of fire, extinguishing by water is possible. Although such mixtures are called "colloidal fuels," the name, though convenient, is not really correct since the normal size of the coal particles is from 1 or 2 to 65μ, whereas the *upper* limit for particles of colloidal dimensions is about $0{\cdot}1\mu$. The first proposal to use coal—oil mixtures as fuel appears to have been made by H. Smith and H. Munsell in 1879, while sporadic experiments in this direction were made from time to time early in the present century. It was not, however, until the matter was taken up by the "Submarine Defense Association" in the United States during the period 1914–18 that serious experimental work on a large scale was carried out. This association, under the chairmanship of Lindon W. Bates, carried out extensive experiments on the production and utilisation of such mixtures, and successful trials were carried out in the U.S. Scout *Gem* between April and July, 1917. Subsequently, trials were made by J. G. Robinson on the firing of locomotives on the Great Central Railway, after which the question of colloidal fuels fell into the background until interest was revived in 1932, when the Cunard liner *Scythia* made the round trip between Liverpool and New York, successfully burning a 40/60 coal—oil mixture in one boiler out of the twelve which are normally fired with oil fuel. Since that date, investigations have proceeded in Great Britain and Germany, chiefly on the *production* of colloidal fuels, but there is very little published information about their combustion.

A colloidal fuel consists essentially of a suspension of solid fuel in a liquid fuel, the mixture being suitably stabilised so that separation of the solid shall not take place under normal conditions of storage and handling at atmospheric temperature during (say) 6 months, or at 100°C. within a few hours.

Such stability may be realised in four ways, by (i) reducing the particle size of the coal; (ii) conferring a gel-structure on the oil by the addition of a suitable stabiliser or "fixateur" to the oil; (iii) using a suitable peptising agent to disperse the coal; or (iv) employing an oil which will give stable suspensions without the addition of a stabiliser or other special treatment.

(i) Although the grinding of coal in oil to colloidal dimensions is quite feasible, the process is costly, and the economic limit of grinding appears to be such that from 80 to 90% will pass through a 200-mesh sieve or perhaps slightly finer.

(ii) It was originally pointed out by S. E. Sheppard in 1921 (J. Ind. Eng. Chem. 1921, **13**, 37) that if the structure of a dilute gel be induced in the oil, coal ground as above (particle size from 64μ downwards) might form a stable suspension in oil. Such a condition may be realised, for example, by suitably dispersing from 0·2–1·0% of sodium stearate in the oil, and it is probable that many other stabilising agents may behave in this manner.

A simple method which appears to be effective consists in blowing air through the heated oil, the stabiliser being then formed by partial oxidation of the oil itself.

(iii) Certain oils, particularly tar oils of high boiling point, possess the power of dispersing bituminous coal when the powdered coal is heated with the oil. The action of tar oils as stabilisers is probably based on this property which, in general, is not possessed by petroleum oils.

(iv) Although, normally, petroleum oils have no dispersing action on coal, the Cunard Co. have found that certain fuel oils, particularly if produced by cracking processes, form stable suspensions with powdered coal without the necessity for the use of any stabiliser. There appears to be a correlation between the carbon residue of the oil and its capability of giving stable suspensions.

An ingenious and simple method of assessing the stability of coal—oil suspensions has been devised by the Fuel Research Board (Ann. Rep. 1935, 155). A sample is placed in a long test tube suspended vertically in a holder so that it may function as a pendulum. The period of swing is noted, and as settlement takes place, the centre of gravity of the pendulum falls, with consequent alteration in the periodic time.

LOW TEMPERATURE CARBONISATION.

The object of low temperature carbonisation of coal is to produce a free-burning, smokeless solid fuel with simultaneous recovery of the smoke-producing portions of the coal as tars, oils and gas. The substitution on a large scale of such a "semi-coke" for the 30–35 million tons of raw bituminous coal at present annually burned for domestic purposes would do much to mitigate the smoke-nuisance, while at the same time products which are now wasted and broadcast into the atmosphere would be conserved. This involves the carbonisation of coal at temperatures ranging from 500 to 650°C., a problem which has so exercised the minds of inventors for the past 30 years that upwards of 200 different designs of plant have been tried for the purpose, but only a few processes have achieved any commercial importance or success.

The serious difficulties presented by this problem are (i) ensuring a sufficiently rapid penetration of heat through the charge of an externally heated low-temperature retort, and (ii) discharging such retorts owing to the fact that many otherwise suitable bituminous coals swell considerably when carbonised at *circa* 500–600°C. And even now the prospects of any large extension of low temperature carbonisation seem doubtful, unless indeed the present price to consumers of the resulting semi-coke can be substantially reduced.

The yields of products obtainable by carbonising a ton of suitable bituminous coal at 500–650°C. will depend partly upon the coal itself and the temperature and largely upon the type of plant employed; in externally heated retorts the yields from typical British bituminous coals, with total volatiles at 900°C.=30–35%, are likely to be as follows: *Gas*—3,500–6,000 cu. ft. of calorific value 600–800 B.Th.U. per cu. ft., or equivalent to (say) 30–40 therms, and containing: CO_2 4–5, CO 4–11, C_nH_m 5, C_nH_{2n+2} (but mostly CH_4) 30–50, H_2 15–30 and N_2 4–5%. *Tar and Oils*—15–20 gallons consisting of (i) *neutral oils* (35–50%) mainly unsaturated hydrocarbons with also some naphthenes and paraffins but little benzenoid hydrocarbons, (ii) *tar acids* consisting chiefly of phenols, and (iii) *bases* (1–2% only). On distillation to 360°C., the tars leave a residue of from 25–40% of soft pitch containing much less free carbon than does that yielded by high-temperature tars. *Light Spirit*—About 3 gallons altogether are obtainable by scrubbing the gas and distilling the tar. *Ammonia*—2–3 lb. (equivalent to about 8 to 12 lb. of sulphate) as a weak liquor, of little commercial value. *Semi-Coke*—About 15 cwt.

The requisites of a satisfactory semi-coke for domestic purposes are that it shall be smokeless, free-burning, low in ash yield, robust enough to withstand handling and transport without undue breakage, uniform in texture, and that its retail price shall be comparable with that of a good house coal. In order to produce a good domestic semi-coke, the coal to be carbonised must have suitable caking qualities, although it by no means follows that a *strongly* caking coal is suitable, because at a carbonising temperature of 500–600°C. strongly caking coals are apt to be highly swelling, and to give a very intumescent and weak semi-coke difficult to remove from the carbonising chamber. The rate of penetration of heat into a charge of coal in a retort is correlated with its tendency to swell, therefore any treatment which will reduce the swelling of the coal will, at the same time, improve the rate of heating. Control of the swelling characteristics may be accomplished either (i) by destruction of any excess of the "binding" constituent over that required to give a strong semi-coke, or (ii) by absorbing such excess by the addition to the charge before carbonisation of a weakly or non-caking coal, or coke-breeze. Destruction of the excess binder may be brought about by partial pre-oxidation of the coal, *e.g.* by heating it in a current of air to about 150°C. ("*Carbocite process*") or alternatively by pre-heating the coal to a temperature of something less than 400°C. for a suitable period. Each treatment has the effect of reducing the caking index of the coal, the first by oxidation, the second by thermal action alone. As, however, the available supply of such strongly coking coals is not unlimited, it seems preferable to reduce proportionally any excess binder present by suitably blending the coal with some appropriate non-coking material such as coke-breeze, or a non-coking coal.

The great variety of the designs proposed for low temperature carbonising retorts has arisen from the desire to improve the heat-transmission and to avoid any trouble from swelling, and in some cases also to ensure larger oil-yields. Broadly speaking, the general line of attack has been in the direction of carbonising the coal either in thin layers, with or without agitation, in externally heated retorts, or in retorts embodying some form of internal heating.

The Parker or "*Coalite*" retort consists of twelve vertical tapered tubes of special cast-iron each 9 ft. long, 4¾ in. diameter at the top and 5¾ in. at the bottom, cast *en bloc* in two staggered rows of six with common gas-collecting chamber and off-take at the top, as shown in Fig. 3 (Bone and Himus, *op. cit.*), and a chamber at the bottom in which the semi-coke from each charge cools during carbonisation of the succeeding charge. The retorts are usually set in batteries of 32 and heated by gas burnt in combustion chambers built between the retorts so that no flame comes into contact with the retorts. As shown in Fig. 3 hot air enters the setting through the duct A and ports B, while gas enters through the firebrick burner C and holes D. The combustion is completed when the heating gases enter the main flue E, which contains a recuperator to pre-heat the combustion air; the charge per retort is about 6 cwt. and carbonisation occupies from 3½ to 5 hours, depending on the coal used and the temperature of the heating chamber, which may vary from 500 to 700°C. The rich gas from the retorts passes to an electrostatic precipitator for the removal of oil and mist. Ammonia is next removed in an acid-washer, which is followed by a water-cooled condenser. After passing through an exhauster, the gas is scrubbed for the recovery of light spirit, and finally passes to a storage holder.

The yields per ton of suitable coal are approximately: Coalite, 14 cwt.; coal oil, 18 gallons; crude spirit (scrubbed from the gas), 2½ gallons; ammonia, 3–4 lb.; gas, 4,000–5,000 cu. ft. of about 750 B.Th.U. per cu. ft., or 30–37·5 therms, of which about 25 therms would be required to effect the carbonisation. Four large plant are operating: (i) at Barugh, nearly Barnsley, consisting of 5 batteries of 32 retorts each; (ii) at Askern Main colliery near Doncaster, where there are 6 batteries each of 36 retorts; (iii) the East Greenwich works of the South Metropolitan Gas Co., consisting of 5 batteries, each of 36 retorts; and (iv) at Bolsover, Derbyshire, where there are 288 retorts. By far the greater part of the semi-coke made in Great Britain is produced by these plant.

The Fuel Research Board have developed a "slot" type of vertical retort 7 in. by 6 ft. 6 in. at the top, tapering to 11 in. by 6 ft. 6 in. at the bottom and 21 ft. high. The retort is built of firebrick, and has been worked at temperatures from 600 to 700°C.; it may be operated either continuously or semi-intermittently. The through-put may be as much as three times that attained with a cast-iron retort of the same dimensions operated at 600°C., the yields of tar and gaseous therms being both materially increased at the expense of the semi-coke. Experiments have been carried out with all kinds of coals, the through-put per retort per day being from 5 to 10 tons according to whether strongly or weakly coking coal is being treated. The heat in-put required to carbonise 20 tons of medium-coking coal per day in two such retorts is remarkably low, being only 19·8 therms per ton.

The Babcock and Wilcox retort is an example

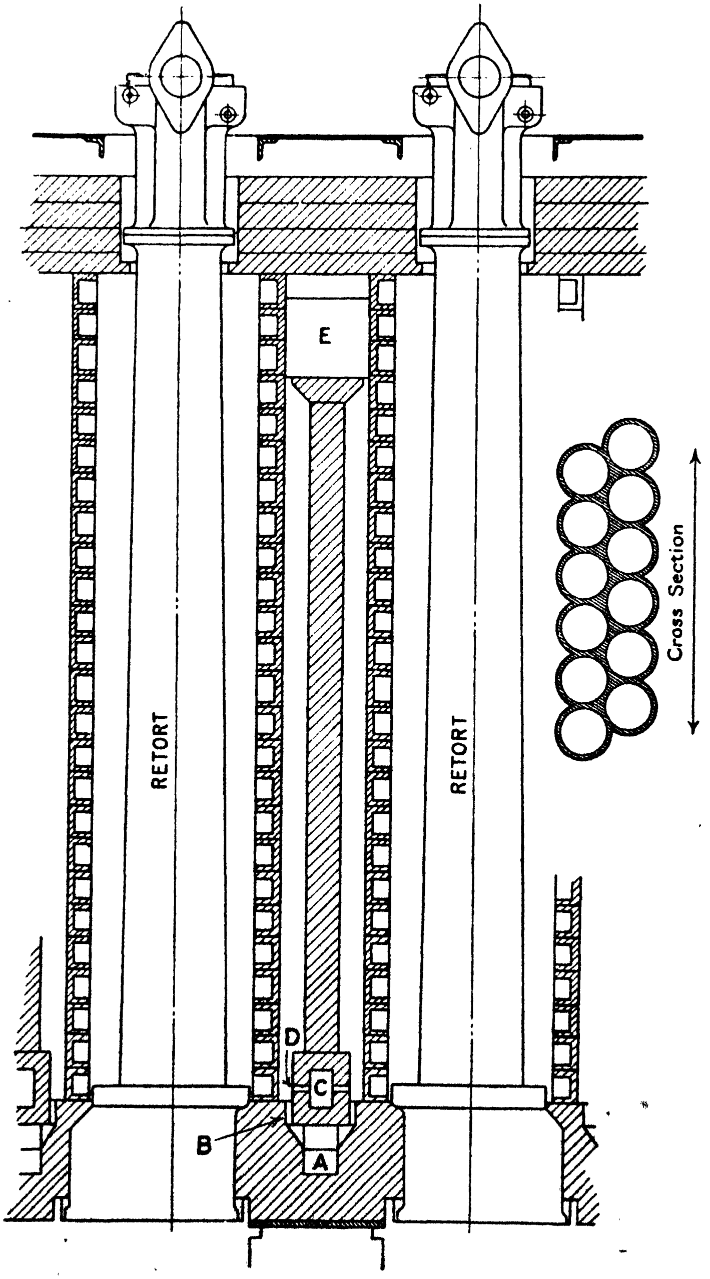


Fig. 3.—The Parker or "*Coalite*" Retort.

of a plant in which internal heating is practised, preliminary treatment of the coal to modify its swelling characteristics being also applied. The coal is first preheated to 130°C. for about 15 minutes on a chain-grate stoker by means of hot gases from a special combustion chamber, and is then discharged *via* sealing valves on to a scraper-conveyor which distributes it uniformly over the surface of the fuel bed in the rectangular retort below. The fuel bed is about 3 ft. deep and is supported on six hydraulically-operated rollers of special cast-iron, which continuously discharge the semi-coke into hoppers from which it is passed over rotary screens on which it is quenched. Carbonisation is carried out by passing superheated steam and hot combustion products (from the burning of the gas generated in the process) at a temperature of between 600 and 700°C. The volatile products are passed through an appropriate recovery plant, and after removal of light spirit the scrubbed gas is finally returned to the plant for heating the retort. The yields obtained per ton of coal in a test carried out by the Fuel Research Board in such a retort when carbonising 29·8 tons of Hartley Smalls per day were : semi-coke, 15·04 cwt.; tar, 16·8 gallons; light spirit (from gas), 2·6 gallons; gas, 38,700 cu. ft. of 27 gaseous therms.

Semi-coke is an excellent domestic fuel; readily ignited and smokeless, the radiant efficiency is about one-third higher than that of coal and slightly above that of anthracite or high-temperature coke. Assuming good house coal and semi-coke to cost 50*s.* and 60*s.* per ton respectively, the approximate costs of radiant heat per therm are 8·9*d.* from coal and 8·0*d.* from semi-coke.

Low-temperature tars, by reason of their content of phenolic bodies (approximately 30%) have a relatively low calorific value, from 15,500 to 15,600 B.Th.U. per lb. compared with 18,600 to 19,600 B.Th.U. per lb. for crude petroleum. They form, however, good raw material for hydrogenation and may thus be converted to motor spirit (free from tar acids) and Diesel oil, the yield of motor spirit under suitable conditions being up to 75%.

The following statistics apply to the British low-temperature carbonisation-industry in 1935 : coal treated, 0·33 million tons; semi-coke produced, 0·26 million tons; tar produced, 5·3 million gallons; crude spirit scrubbed from gas, 0·88 million gallons ; gas produced, 1,658 million cu. ft., equivalent to a yield of 32·3 therms per ton of coal.

HIGH TEMPERATURE CARBONISATION.

Coke is the solid product of the high temperature carbonisation of coal. It varies considerably in external character. For metallurgical purposes, the best coke is compact, heavy, homogeneous, with bright light-grey surface. It contains, besides carbon and ash, small quantities of hydrogen (0·2–1·2%), oxygen (traces and up to 1 or 2%), and organic sulphur (total S 0·8–1·8%). The best cokes contain upwards of 90% of carbon, less than 8% of ash, and should have a metallic ring. Coke is only slightly hygroscopic, and when thoroughly dried does not absorb more than 1–2% of moisture from the atmosphere. The moisture in coke put on the market should not exceed 3%. The calorific value of dry coke containing 90% of carbon and 0·5% of hydrogen is about 7,450 K.C.U. per kg. (13,410 B.Th.U. per lb.). The greater portion of the coke manufactured at coke oven plants is disposed of for metallurgical purposes, while that made at gasworks (after the requirements of the works for heating the retorts and for production of water-gas have been supplied) finds a ready sale to industrial and domestic consumers. The latter market has expanded to such an extent during recent years that in 1937 there was a shortage of supplies. For further details, *see* COKE MANUFACTURE and GAS, COAL.

Gasification of Coal. (*a*) *Producer-Gas.*—For the cheap and rapid production of gaseous fuel for industrial purposes, there is no better process than the gasification of solid fuels (peat, bituminous coal, coke or anthracite) by means of a mixed air–steam blast (sometimes air alone is employed) in some form of gas " producer," whereby the fuel is converted into gas containing some 35–45% of combustible constituents (CO, H and CH_4). A modern gas producer consists of a cylindrical furnace, 6–12 ft. internal diameter and 10–15 ft. high, lined with fire-brick with an outer mild steel casing, and usually water-sealed at the bottom. Means are provided (1) for the introduction of the blast through some form of grate or twyer fixed immediately above the level of the water in the seal, and its regular distribution through the bed of incandescent fuel (usually 3–5 ft. in thickness) which rests upon a lower bed of ashes; and (2) for the charging in of the raw fuel through (usually) some form of bell hopper fixed centrally on the top of the producer, round which are arranged a number of equidistant poking holes closed by iron balls. The gas outlet is fixed near the top of the cylindrical furnace. Taking as a typical example a producer working with a mixed air–steam blast on a common bituminous coal, the chemistry of gasification may be epitomised as follows. When a fresh charge of fuel is dropped into the furnace, it first of all undergoes a process of distillation on the top of the fire, whereby H, CH_4, tarry hydrocarbons, CO, together with small quantities of NH_3, H_2S, etc., are evolved, probably in much the same proportions as in the ordinary retort distillation of coal; olefines and higher paraffins are, however, so rapidly decomposed that they do not, as a rule, appear in the gas passing out of the producer. The carbonaceous residue (coke) is subsequently completely gasified in the lower layers of the incandescent fuel-bed, by interaction with the ascending air–steam blast, yielding a mixture of CO_2, CO, H and N, together with further small proportions of NH_3 and CH_4. The proportions of CO_2, CO and H leaving the incandescent coke-bed depend upon the steam-saturation temperature of the blast, which also largely determines the temperature gradient throughout the fire. In order to understand fully the chemistry of the process, it is necessary to consider separately the interaction between incandescent carbon and air and steam respectively. In a solid-bottom producer operated with a *dry*-air blast, the initial action of the oxygen upon the incandescent carbon is rapidly succeeded by the reversible reaction $2CO \rightleftharpoons C + CO_2$ in which the state of equilibrium is a function of both temperature and the partial pressures of the CO and CO_2. It can be demonstrated that the time required for the establishment of this equilibrium, at the temperatures which prevail in the fuel bed, is far shorter than that occupied by the gaseous mixture in traversing the fuel. According to Rhead and Wheeler's experiments (J.C.S. 1910, **97**, 2718), the equilibrium in the system

$$2CO \rightleftharpoons C + CO_2$$

at atmospheric pressure varies with temperature as follows:

	Per cent.	
Temp.	CO_2	CO
850°	6·23	93·77
950°	1·32	98·68
1,050°	0·37	99·63
1,200°	0·06	99·94

results which are in agreement with the thermodynamical equation

$$\frac{19{,}500}{T_{abs.}} + \log_e \frac{C^2_{CO}}{C_{CO_2}} = 20{\cdot}4.$$

As the change from $2CO$ to CO_2 involves a diminution in volume, it can be predicted on thermodynamical grounds that a lowering of the partial pressures of the CO_2 and CO, consequent on dilution with N in the producer gases, will affect the equilibrium in the same direction as an increase in temperature, *i.e.* it will tend to increase the ratio CO/CO_2 at any given temperature. The temperatures in the active zones of the fuel bed of an air-blown producer gasifying coal or coke may vary between 1,250° and upwards of 1,400°, and with good coke it is easily possible to generate a gas containing 0·5 CO_2, 33·0 CO, 1·5 H, and 65·0% N, But since the combustion of carbon to CO liberates approximately 30% of its total heat of combustion, not only would the thermal efficiency of the gasification in an air-blown producer, reckoned on the cold gas, be low, but the high temperatures in the fuel bed would cause serious clinkering troubles in cases where the fuel leaves a fusible ash. In the Thwaite cupola producer (30 ft. high and 6 ft. internal diameter), where a dry-air blast, forced in through a series of twyers near the bottom, is employed, it is usual to add a certain proportion of limestone to the fuel charge in order to form a liquid slag with the ashes, which is tapped at intervals through a slag-notch. Working on a Lancashire slack coal, this producer yields a gas containing 2·0 CO_2, 29·0 CO, 5·35 H, 2·05 CH_4, 61·6 N, of cal. value 130·8 *net*, and 138·7 *gross*, B.Th.U. per cu. ft. at 0° and 760 mm.

Steam reacts with carbon in two ways, namely,

(1) $C + 2H_2O = CO_2 + 2H_2$, and
(2) $C + H_2O = CO + H_2$,

and both reactions are strongly endothermic. At 500–600° (1) predominates; as the temperature rises (2) gradually asserts itself, until at 1,000° and upwards it occurs exclusively. The function of the steam in a gas producer is, therefore, to absorb some of the heat liberated during the partial "air combustion" of the carbon to CO by doing chemical work, thereby raising the potential energy of the resulting gas at the expense of some of its sensible heat. Incidentally, also, clinkering troubles with a fusible ash are greatly diminished by the admixture of steam in the blast. Where a large proportion of steam is used, the composition of the resulting gas is appreciably affected by the reversible system $CO + H_2O \rightleftharpoons CO_2 + H_2$, of which the equilibrium constant,

$$\frac{CO \times H_2O}{CO_2 \times H_2} = K,$$

increases with temperature (according to O. Hahn, K=0·81 at 786°, 1·54 at 986°, and 2·10 at 1,205°). The operation of this reversible reaction must also be considered when a producer gas passes through the hot regenerators of an open-hearth furnace.

The influence of varying blast-steam saturation temperatures upon the composition and yield of the gas from a Lancashire bituminous coal containing C 78·0, H 5·4, S 1·0, N 1·4, O 10·0, ash 4·2%, and yielding 36% volatiles at 900°, is shown in the tabulated results at the top of the next page of a series of gas-producer trials (each extending over a continuous period of 100–130 hours) carried out by Bone and Wheeler in 1906–7 (J. Iron and Steel Inst. 1907, i, 126 1908, ii. 206).

In these trials it was also proved (1) that on gasifying an ordinary bituminous coal by means of a mixed air-steam blast, about 92·5% of the carbon in the fuel is converted into permanent gas (CO_2, CO and CH_4), another 6·3% appears as tar, and the remaining 1·2% is lost in the ashes. These proportions are independent of the blast-steam saturation temperature. (2) That with blast-steam saturation temperatures up to and including 55°, the whole of the steam in the blast is decomposed in passing through the fuel bed; as the saturation temperature is raised above this limit, the proportion of the steam decomposed progressively diminishes, although the absolute quantity (per lb. of fuel) increases. (3) That increasing the effective depth of fuel bed beyond 3 ft. 6 in. has no influence upon either the composition of the gas or the practicable rate of gasification. (4) That the thermal efficiency of the gasification reaches a maximum at blast-steam saturation temperatures between 50° and 60°, and that the best quality of gas for furnace purposes is produced with a saturation temperature of 50°.

In gas generated for furnace purposes it is important that the CO content should be as high as possible, and that the H content should not exceed about 12–14%; moreover, for a regenerative furnace-supply the gas leaving the producer should be in a hygroscopic condition such that the proportions of CO_2, CO, H and H_2O shall substantially conform to the equilibrium *ratio* corresponding to the highest temperature of the regenerator (say 1,200°), namely,

$$\frac{CO \times H_2O}{CO_2 \times H_2} = 2{\cdot}0.$$

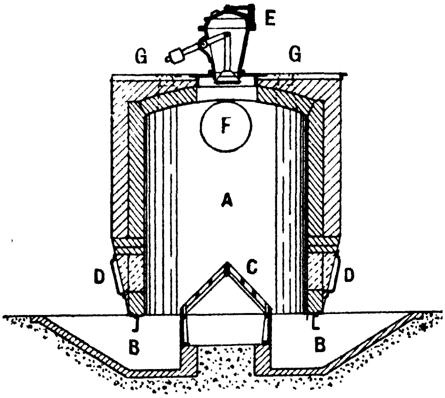
Average depth of incandescent fuel . .		3 feet 6 inches.					7 feet.				
Average rate of gasification (day-shift) per hour per producer .		22·5 cwts.					11·5 cwts.				
Steam-saturation temperature of blast . .		45°	50°	55°	60°	70°	60°	65°	70°	75°	80°
Percentage composition of the gas.	Carbon dioxide	2·35	2·50	4·40	5·10	9·25	5·25	6·95	9·15	11·65	13·25
	Carbon monoxide . .	31·60	30·60	28·10	27·30	20·85	27·30	25·40	21·70	18·35	16·05
	Hydrogen . .	11·60	12·35	15·45	15·50	19·75	16·60	18·30	19·65	21·80	22·65
	Methane . .	3·05	3·00	3·00	3·05	3·45	3·35	3·40	3·40	3·35	3·50
	Nitrogen . .	51·40	51·55	49·05	49·05	46·70	47·50	45·90	46·10	44·85	44·55
	Total combustibles	46·2	45·95	46·60	45·85	44·05	47·25	47·10	44·75	43·50	42·20
Calorific value of the gas, B.Th.U. per cubic foot at 0° and 760 mm.	Gross	180·0	178·5	180·8	178·7	175·5	185·6	185·4	177·5	172·0	169·5
	Net	170·5	168·7	169·1	166·9	161·0	173·0	172·0	163·3	157·3	154·3
Yield of gas, cubic feet, at 0° and 760 mm. per ton coal . . .		133,700	132,500	132,700	135,000	—	138,250	134,400	141,450	145,800	147,500
Steam added to blast, lbs. per lb. coal . .		0·2	0·21	0·32	0·45	--	0·45	0·55	0·80	1·10	1·55
Percentage steam decomposed		100	100	100	76·0	--	87·0	80·0	61·0	52·0	40·0

This latter requirement is fulfilled by a gas containing 2·5 CO_2, 30·6 CO, 12·35 H (such as may be generated with blast-steam saturation temperature of 50°), and leaving the producer in a hygroscopic condition corresponding to saturation at 20°. Such a gas will leave the producer heavily charged with tarry vapours, and at a temperature of 500–600°; it usually passes on to the furnace through large mains lined with fire-brick, without being cleaned or cooled, accumulations of tar, soot, etc., in the mains being burnt out in a current of air at the end of each week's run (*v. also* W. A. Bone, "Producer Gas, with special reference to Steel Works Requirements," Journ. W. of Scotland Iron and Steel Institute, 1911).

In gas generated for power purposes, the actual composition is not so important, provided that the total content of combustible constituents is high, and in such cases the gas may be generated under conditions permitting of the recovery of a large proportion of the N in the fuel as NH_3. A gas supply for internal-combustion engines must be both thoroughly cleaned and cooled down to atmospheric temperature before delivery to the engine.

The main points to be considered in relation to gas-producer design are: (1) the easy and accurate control of the blast-steam saturation temperature; (2) a suitable form of grate or twyer which should permit of a rapid rate of gasification, together with uniform distribution of the blast, through the fuel bed; (3) the contour of the furnace body; and (4) the arrangements for charging the producer and removal of the ashes. One of the earliest forms of gas producers (Ebelmen, 1840) was of the cupola type, in which charcoal or coke was gasified, with a positive blast introduced through twyers, limestone being added to the charge (if necessary) to flux the ash. In 1845 Ekman, a Swedish ironmaster, designed a furnace and producer combined, for which the fuel was charcoal. The producer itself consisted of a cylindrical fire-brick chamber, enclosed in an iron casing, a space being left between the brickwork and the casing through which the air supply was admitted and preheated on its way to the fire. In 1861 the brothers Siemens patented their well-known producer for use in connection with their new regenerative furnace. This producer consisted of a fire-brick chamber, rectangular in section, the front of which was inclined at an angle of 45–60°, provided with a grate at the bottom, through which a current of air was induced. Below the grate was a trough of water, which, on evaporation, by heat radiated from the grate, added a certain proportion of steam to the induced air supply. Subsequently the front of the producer was closed by an iron door, and the air supply forced in under the grate by steam injection. This producer was the first to successfully gasify a bituminous coal; it was capable of generating a fairly good quality of gas, but its rate of gasification was low. In 1876 Messrs. Brooke and Wilson patented a producer consisting of a cylindrical chamber having a solid hearth, but no fire bars. The mixed air–steam blast was obtained by steam injection, and was introduced into the fuel bed by means of a box-shaped casting which traversed the middle of the hearth. In 1882 Mr. Wilson patented a form of generator on which ash and clinker were automatically removed by means of two worm screws revolving in a water seal. Water-sealed producers have now almost entirely superseded the older solid or bar-bottom types.

The Duff producer (Fig. 4) may be cited as a wet-bottomed producer of simple design; it consists of a cylindrical chamber A, 7–10 ft. internal diameter, with a 9-in. fire-brick lining within an outer steel shell. At the bottom of the lining is a circular angle-iron casting, which dips into the water seal in the trough BB. The "Duff" grate, or blast grid, C, is a ∧-shaped structure, with transverse grids extending as a ridge across the producer immediately above the water seal; the air-steam blast enters the space beneath the grate, and the grid ensures its uniform distribution over a considerable area of the fuel bed. The latter (which, as a rule, extends to a height of about 3 ft. above the apex of the grate) is supported upon a bed of ashes, which extends downwards from the grate level into the water trough. In the lower part of the shell of the producer, and on a level with the grate, cleaning doors DD are provided. The fuel is charged intermittently into the furnace through the belled hopper E, and the gas outlet is at F; the dotted lines at GG indicate poking holes. Ashes are withdrawn from the water trough at regular intervals in quantity corresponding to the rate of accumulation in the furnace. A producer of 10 ft. internal diameter will gasify 10 cwt. of coal per hour, or about 15 lb. per sq. ft. of fire area.



SECTION THROUGH WATER SEAL.

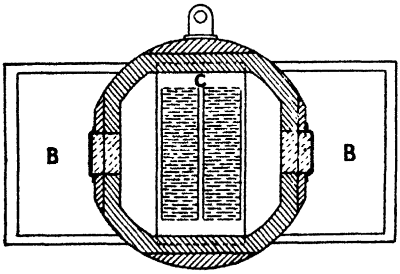


Fig. 4.

In Fig. 5 is shown one of the earlier forms of the Mond producer, which, although designed with special reference to ammonia-recovery practice, is eminently adapted to all working conditions. The chief features about this producer are (1) the annulus A between the inner fire-brick lining and outer steel shell through which the incoming preheated air-steam blast passes before reaching the grate; (2) the hanging bar grate B, which takes the shape of an inverted truncated cone, with spaces between the bars for the admission of the blast, an arrangement which ensures an adequate grate area and a very uniform and effective distribution of the blast in the fuel bed; and (3) the large bell C at the top of the producer below the charging hopper D, which is supposed to expedite the preliminary distillation of the raw fuel. The Mond producer is usually worked with a very deep fuel bed, as indicated in the diagram, but if the bell C be dispensed with, a much shallower fuel bed may be used with advantage.

To secure the best results from a gas producer, continuity of operation is essential; the coal should be charged regularly, in small quantities and evenly spread over the fuel bed. Irregular charging of coal in large quantities results in sudden chilling of the upper layers of the fuel bed and, in consequence, increased CO_2 in the gas. Furthermore, it is desirable that the removal of ash and clinker should take place with minimum disturbance of the fuel, since this tends to channelling of the bed, while small pieces of clinker are liable to be lifted into the active combustion zone where they would tend to grow by accretion.

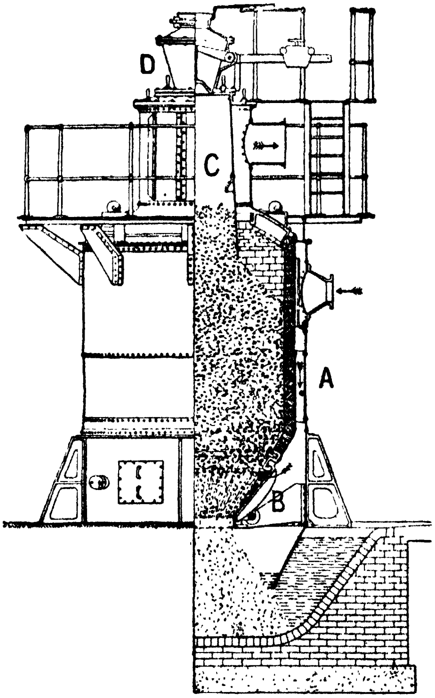


Fig. 5.

The Morgan "Gas Machine," which is largely used in steel works, is illustrated in Fig. 6. The object of the plant is to carry out gas making with minimum disturbance of the fuel bed. The body of the producer and the ash-pan are revolved mechanically, the top remaining stationary, a water seal ensuring a gas-tight joint. Coal is continuously fed into the producer by a drum which is divided into quadrants and by reason of the fact that the fuel bed revolves, is distributed over the surface thereof. The surface of the fuel bed is continuously levelled by two water-cooled levelling bars suspended by trunnion-joints from the top plate of the producer.

The air-steam blast is admitted *via* a central mushroom-shaped twyer. The ash-removal device consists of a spiral bar ending in an ash-plough which revolves with the producer. When it is required to remove ashes, the plough with the spiral bar is stopped for one complete revolution of the producer, and then automatically released to revolve again with the producer.

Such a producer, 10 ft. in diameter, will gasify 3,000 lb. of coal per hour, the power consumption being only ¾ brake horse-power.

The Power Gas Corporation's Mechanical Producer-Gas Plant.—One of the latest power-gas producers with automatic feeding and ash discharge is shown, together with its gas-cleaning accessories, in Fig. 7. It consists of a steel shell, the upper part of which is lined with refractory brick, while the lower portion is provided with a water-jacket which functions not only as a boiler in which the steam necessary to saturate the blast is generated, but also as a cooling agent round the primary combustion zone which tends to prevent formation of clinker on the walls.

The Koller grate which is concentric with the producer shell is built up of special cast-iron rings, superposed one above the other, the space between forming horizontal ports for the even distribution of the blast. The grate is securely bolted to the revolving ash-pan, the floor of which slopes outwards. Spiral ribs, which are cast on to the ash-pan, shear the bottom from the column of ash and force it outwards under the cast steel seal ring which carries several ash hooks against which the larger masses of clinker are broken up. The ash is automatically discharged over a steel plough bolted to the seal ring, the equal spacing of the ash hooks round the ring ensuring its even removal. Fuel is charged to the producer by means of a mechanically-operated feeding device.

When coal is gasified in the producer the hot, crude gas contains both dust and tarry matter. For firing certain furnaces the hot, crude gas can be utilised as such; but for other purposes the gas must be cleaned.

In the producer plant illustrated, the hot, crude gas is first passed through a Lymn washer in which it is cooled by means of water sprayed in at the top of the tower and dust and some of the tar are removed.

The Lymn washer consists of a tower with a vertical stationary shaft located in the centre, fitted with a series of distributing cones at suitable distances from each other functioning in conjunction with a corresponding series of inverted truncated cones attached to the casing and serving as collecting devices. Water is sprayed in at the top of the tower and gas enters at the bottom. Thin sheets of water fall alternately from the distributors to the collectors and *vice versa* and are atomised in the form of a fine spray actually driven by the gas—itself flowing in a zig-zag path in the opposite direction—on to the collectors or distributors where the spray again forms into sheets of descending water. The whole of the gas is thus brought into contact with the water several times before leaving the tower.

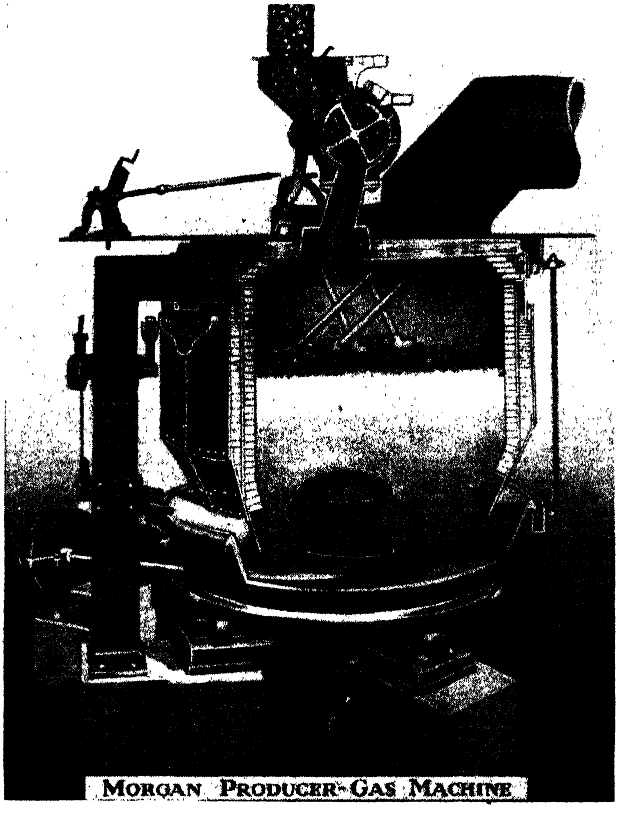


FIG. 6.

After leaving the washer, the cooled gas passes

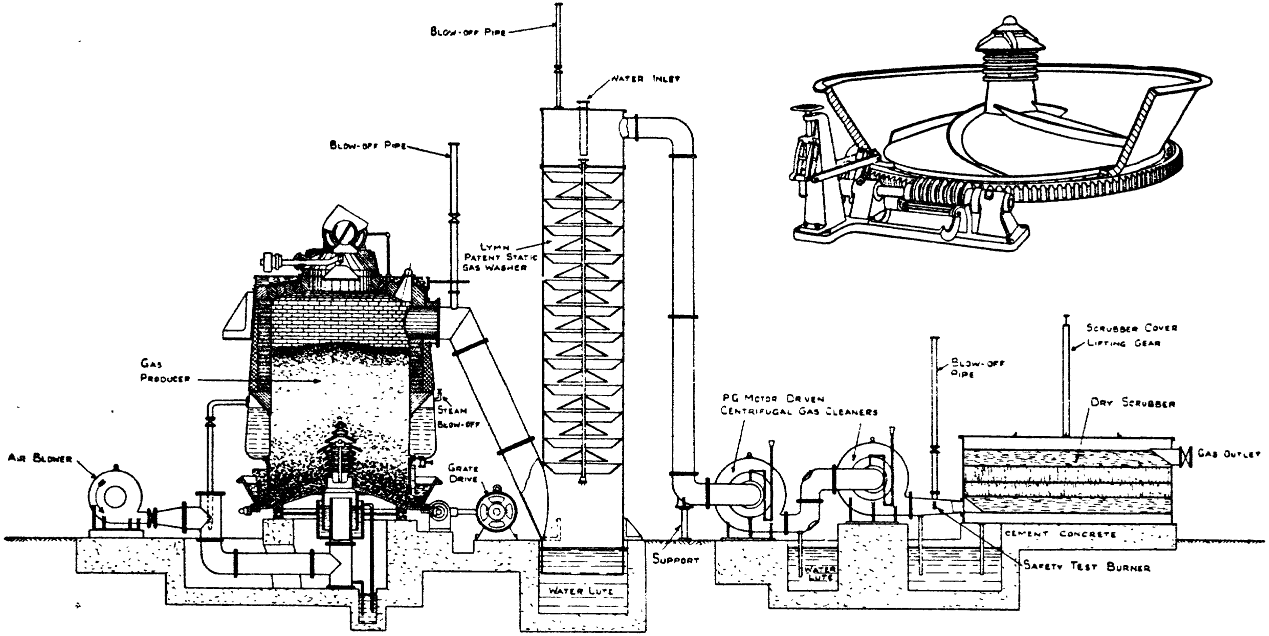

Blow-off Pipe
Water Inlet
Blow-off Pipe
Lymn Patent Static Gas Washer
Gas Producer
Steam Blow-off
Air Blower
Grate Drive
Water Lute
Support
P.G. Motor Driven Centrifugal Gas Cleaners
Blow-off Pipe
Scrubber Cover Lifting Gear
Dry Scrubber
Gas Outlet
Water Lute
Cement Concrete
Safety Test Burner

FIG. 7.

into gas cleaning fans, in which it comes into contact with a fine spray of water which causes the fine dust and tar particles to coalesce and settle out. Final cleaning is carried out in a dry scrubber, this consists of a box containing perforated trays which are packed with wood shavings. The wood shavings act as a filtering medium and the finest particles of tar are removed from the gas, which is then cold, clean and suitable for all industrial and power purposes.

The composition of the gas obtainable when gasifying bituminous coal (nut size), with the blast-steam saturation temperature about 62°C., is:

CO_2 5·0, CO 28·2, H_2 15·3, CH_4 3·2, N_2 48·3%.
Calorific value (gross) = 183 B.Th.U. per cu. ft. at N.T.P.

Several other leading makers of producers have successfully designed similar mechanical revolving grates for the automatic removal of ashes and these have been employed on large installations in steel works and the like.

For the cleaning and cooling of producer gas for gas engines, various arrangements of plant are employed, comprising usually (1) a dust-catching chamber, (2) atmospheric condensers, usually of annular type, (3) water-sprayed coke or "hurdle" scrubbers, (4) water-sprayed fans or tar extractors, and finally (5) sawdust scrubbers or other equivalent devices for removal of tar fog.

Blowing Arrangements.—All large gas-producers are blown on the pressure system, either by means of steam injection or, preferably, by a suitable fan or blower, steam or electrically driven. The pressure required is usually only from 3 to 6 in. water gauge, according to the thickness of the fire. In the case of a blower-produced blast, the requisite steam is introduced through a lateral opening into the air duct a few feet before it enters the producer. Perfect control and adjustment of the steam-saturation temperature of the blast is of the utmost importance from the point of view of efficient and uniform working.

For small (up to 200 H.P.) power installations, producers in which the blast is induced by the suction of the engine cylinder ("suction producers") are now largely employed with anthracite or coke as fuel. The first successful attempt to operate a producer by suction in conjunction with a gas engine was made by Léon Bénier in 1896, who employed a suction pump, placed side by side with the engine cylinder and driven by means of a connection with the fly-wheel axle. Soon afterwards the suction stroke of the engine itself was substituted for the Bénier suction pump, thus cheapening construction and at the same time reducing frictional losses.

By the year 1901 "Suction-Gas Plant" were established on the market. Such a plant (as illustrated in Fig. 8) consists of the following essential parts: (1) a generator A of cylindrical section lined with fire-brick in which the fuel is gasified by means of an air–steam induced draught. The fuel is introduced through an air-tight feeding hopper B, which drops it into a storage and distillation bell C, situated within the generator. The fire rests upon a horizontal grate under which is a shallow chamber, D, with a solid bottom, and a lateral opening communicating with the air and steam supplies. (2) A vaporiser, E, fixed either within or without the upper part of the shell of the generator, in which a regulated water supply is vaporised, usually at the expense of some of the sensible heat of the hot gas leaving the generator, or sometimes by the heat of the fire. (3) A water-sprayed coke-scrubber, F, for cooling and washing the gas, and (4) an expansion box G, which serves the double purpose of a gas reservoir for the engine, and, on the suction stroke, of minimising the pulsations.

The generator is started up by kindling a wood fire on the grate with a layer of coke or anthracite above. The fire is blown up by means of a hand fan, which is a necessary auxiliary to the apparatus. During the starting-up period the products of combustion are sent into the atmosphere through a vent pipe, but as soon as a rich enough gas is generated (about 20–30 minutes from the start) the engine is started and the fan is shut off.

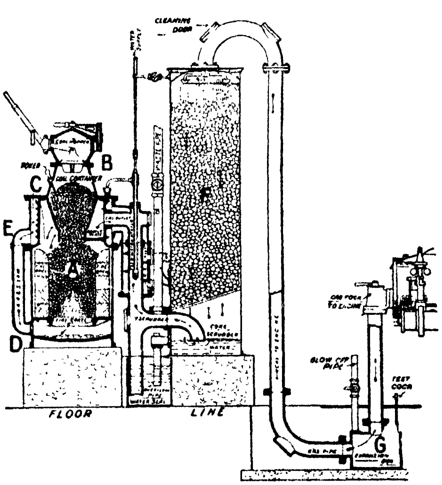


FIG. 8.

A typical "suction gas," generated from gas coke, with air saturated with steam at 51·7°C., contained

CO_2 5·15, CO 25·45, H_2 13·10, CH_4 0·30 and N_2 56·00 %,

its net calorific value being 127 B.Th.U. per cu. ft. at 0°C. and 760 mm.

The thermal efficiency of the gasification, allowing for the power required to draw the gases through the system, and based on the net calorific values of the coke and gas respectively, is about 78·5%. The fuel consumption on a suction plant is about 1 lb., or even slightly less, per B.H.P. developed, the water consumption for scrubbing the gas being about 1·2 gallons per B.H.P.

Ammonia Recovery Systems.—In 1889 Ludwig Mond, in his Presidential Address to the Society of Chemical Industry, described how he had evolved a new system for generating producer-gas from bituminous coal slack under conditions which permitted the recovery of as much as 70·6 lb. of ammonium sulphate per ton. The best practical results are obtained by working the producer with a blast-steam saturation temperature of 85°C., the mixture of air and steam being pre-heated to about 250°C. before it enters the fuel bed. There is carried into the producer by the blast about 2 lb. of steam for every 1 lb. of coal gasified. One-third only of this steam is decomposed by interaction with carbon in passing through the fuel bed, the remaining two-thirds passing with the hot gases out of the producer. The outstanding features of the process are (1) that, owing to the cooling influence of the large proportion of steam in the blast upon the fuel bed, the low temperature interaction

$$C+2H_2O=CO_2+2H_2$$

predominates over the high temperature reaction, $C+H_2O=CO+H_2$, so that the resulting gas has a high hydrogen and low carbon monoxide content as compared with ordinary producer gas; and (2) that for economical working it is necessary that the large proportion of steam leaving the producer shall be conserved to the system by some efficient recuperative arrangement. From a coal containing between 1·2 and 1·6% of nitrogen, it is possible to obtain up to 90 lb. of ammonium sulphate per ton, together with up to 150,000 cu. ft. of gas (at 0° and 760 mm.), of calorific value about 150 gross and 135 net B.Th.U. per cu. ft. at 0° and 760 mm., containing:

CO_2 17·0, CO 11·0, H_2 24·0, CH_4 3·0 and N_2 45·0%.

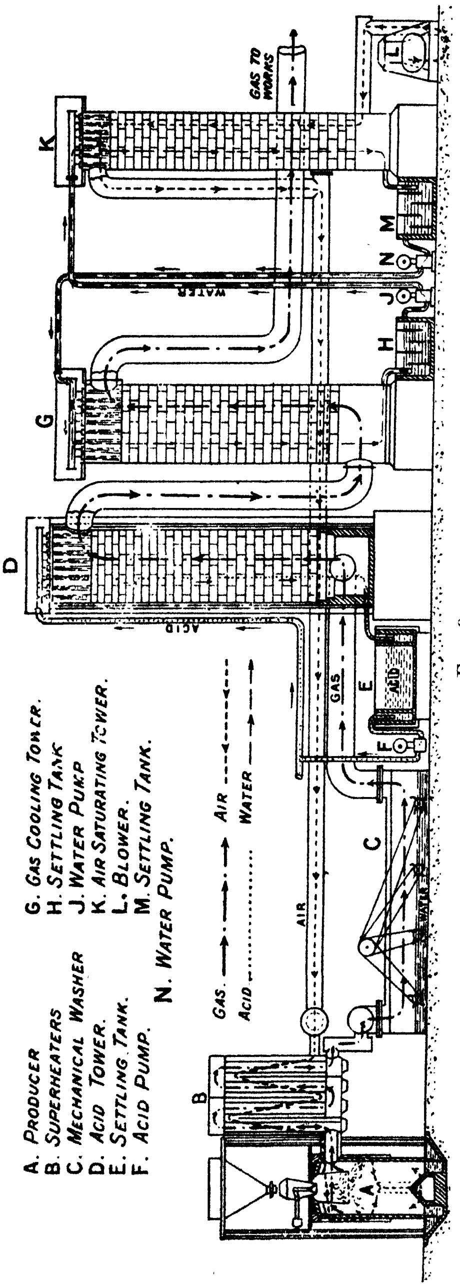


Fig. 9.

In the original *Mond System of Ammonia Recovery* and steam recuperation, the gas left the producer heavily charged with steam and tarry vapours at a temperature usually between 500 and 600°C. It then traversed the central tubes of a series of three annular "Superheaters," indicated by B in the diagram (Fig. 9), each about 20 ft. long. The incoming steam–air blast passed through the annulus between the central and outer tubes in the reverse direction. The temperature of the gas was thus reduced to between 300 and 400°C., while that of the blast was raised to about 250°C. Further superheating of the blast occurred as it subsequently traversed the annulus between the inner and the outer steel casings of the producer itself. The partly cooled gas next passed through a long rectangular and water-sealed chamber (the "mechanical washer") C, where it encountered a water spray thrown up by a series of revolving dashers, by which means dust, soot and a large amount of heavy tar were removed, and the gas itself was further cooled to about 100°C. It next passed up the lead-lined scrubbing tower D, packed with perforated bricks or tiles, down which an acid liquor containing ammonium sulphate plus 2·5% of sulphuric acid was sprayed, the volume of liquor being so adjusted in relation to the upward flow of gas that the latter left the tower at a temperature of 80°C. and free from ammonia. The liquor from the bottom of the tower, D, ran into an open tank provided with suitable partitions, in order to eliminate from it any small quantity of surface tar. To the main bulk of the circulating liquor was added a regulated quantity of sulphuric acid, after which it was again pumped up to the top of the acid tower D. A portion of the liquor was, however, removed from the circuit and evaporated to crystallising point in a special vacuum evaporator heated by means of steam pipes. After separation of ammonium sulphate, the mother liquor was pumped back into the main liquor circuit. The ammonia-free gas, on leaving the acid tower at 80°C., was passed up the "gas-cooling tower" G, where it encountered a downward spray of cold water, so regulated that, while the gas was cooled to about 60°C., the water was heated to between 75 and 78°C.

The gas passed thence onwards to the place of consumption, a second water-sprayed cooling tower being previously used in order to cool the gas to 30°C., at which temperature it contained only 4% by volume of water vapour. When, however, the gas was intended for engines, it was further cooled to within a few degrees of the atmospheric temperature, and was also passed through a sawdust scrubber to remove last traces of tar.

The hot water from the "gas-cooling tower" was passed through a tar separator, after which it was pumped up to the top of the "air-saturating tower" K, down which it was sprayed. The air blast for the producer was forced up this tower by means of a blower. In this way the blast was heated to, and saturated with steam at 75°C., at the expense of the hot water. A further quantity of live steam was added to the air blast as it passed forward to the superheaters in order to raise its steam-saturation temperature to 85°C. The chief drawback of the original Mond System was the large capital outlay involved, which rendered ammonia recovery unprofitable unless either the amount of coal gasified exceeded about 180 tons per week or the fuel was very cheap and contained more than 1·5% of nitrogen. Moreover, the gas, being rich in hydrogen and poor in carbon monoxide, was not well suited for open-hearth steel- or glass-melting-regenerative furnaces. Successful efforts have been made to reduce the capital cost of the plant by substituting the expensive lead-lined vertical acid tower by rectangular horizontal washers, constructed of steel or iron work and rendered resistant to the acid liquor by special treatment, and numerous Mond plant on these modified lines have been erected.

In the *Power Gas Corporation or Lymn System* the hot crude gas passes through a vertical dust washer 1 (Fig. 10) in which it is cooled by hot water nearly to its dew point, and the bulk of the dust is removed. It then passes to a Lymn washer 2, in which it is washed with a liquor containing a little free sulphuric acid, and this removes the ammonia at an absorption efficiency of 95–99%. The top of the washer is provided with a coke filter to prevent the carrying forward of acid spray. The hot gas is next washed with water in Lymn washer No. 3, from which the hot water passes directly into washer No. 5, in which it is cooled by the air on its way to the producers, the air thus becoming simultaneously saturated with moisture and heated. Final cooling of the gas is carried out in Lymn washer No. 4, and the gas washing fans 6, one of which may be supplied with absorbing oil to remove light spirit. If for use in gas engines or small furnaces, the gas is passed through sawdust scrubbers 7. The solution of ammonium sulphate from 2, when of sufficient strength (sp.gr. 1·18–1·2) is passed to a storage tank 13, and thence to the vacuum evaporator 14, from which the salt is delivered to the centrifugal dryer 16. Nos. 8 and 9 are tanks and pumps respectively for circulating the liquor and water; 10 is a tank for the storage of tar, which is subsequently dehydrated to about 2% moisture in 11, from which it is charged into barrels, 12. 15 is a jet condenser in which the vapour driven off from

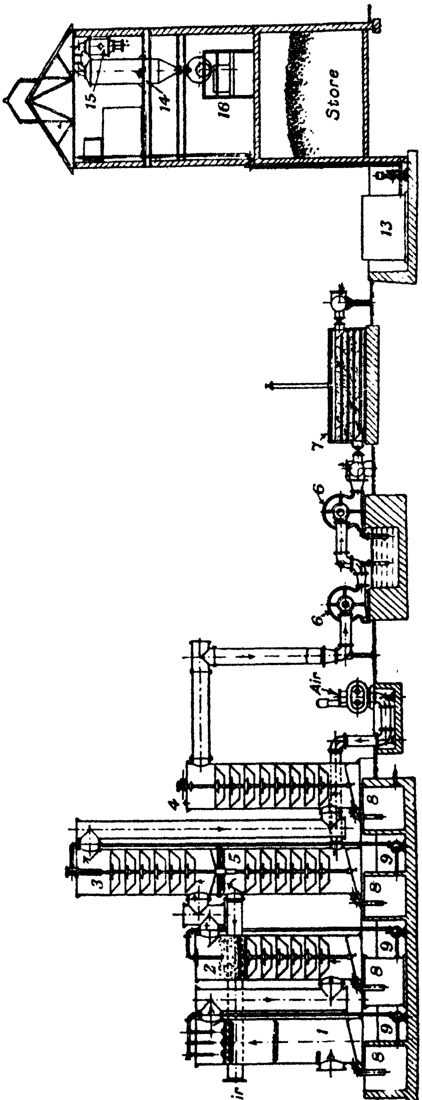


FIG. 10.—THE POWER GAS CORPORATION (LYMN) SYSTEM OF AMMONIA RECOVERY.

the liquor in 14 is condensed. The air-blast to the producer is taken into the system by a blower, saturated with water vapour as already described, and finally pre-heated at the expense of part of the sensible heat in the gas from the producer.

In the *Power Gas Corporation Low Temperature System*, the producer is operated with a very deep fuel bed (about 50% greater than in the Mond plant) so that (*a*) the coal in the upper part of the fuel bed is subjected to low temperature carbonisation by internal heating, and (*b*) the time of contact of the steam with the fuel is increased, leading to lower steam-requirements for a given recovery of ammonia, higher thermal-efficiency of the process, higher yield of tar and improved quality of gas. The chief modifications in the producer are an increase in height relative to the diameter and adaptation of the gas offtake.

TYPICAL RESULTS OBTAINED IN THE MOND AND POWER GAS CORPORATION LOW TEMPERATURE PROCESSES.

Assumed fuel analysis. Volatiles 37·0, Ash 12·0, N 1·4%. Net calorific value = 12,000 B.Th.U. per lb.

	Mond.	Power Gas Corporation Low Temperature.
Gas.		
Cu. ft. per ton	133,500	118,000
CO_2%	16·0	8·3
CO%	11·0	20·5
H_2%	25·0	20·5
CH_4%	2·7	5·5
N_2%	45·3	44·9
Calorific value. B.Th.U. per cu. ft. net at N.T.P.	136	182
Ammonium sulphate recovered.		
Lb. per ton	90	90
Tar. Gallons per ton.	10	21
Thermal efficiency of producer.		
Including tar	74	92·3
Excluding tar	68	80
Steam, from outside sources, required per ton of coal. Tons	1·9	1·05

Water-Gas *v.* GAS, WATER.

Blast-Furnace Gas.—The blast-furnace, by virtue of its mode of operation, inevitably behaves as a huge gas-producer, upwards of 50% of the potential heat in the coke leaving the furnace as potential heat in the blast-furnace gases, and in consequence, much attention has been paid to the efficient utilisation of such heat. The composition of gas issuing, at 250–300°C., from a modern coke-charged blast furnace under normal smelting conditions will usually be within the following limits:

CO_2 10–13, CO 26–30, H_2 1–2 and N_2 58–60%.

Its specific gravity is practically the same as that of air; its gross calorific value when *dry* may be taken as practically 100 B.Th.U. per cu. ft. (or about 880 kg.-cal. per cu. metre) at 0°C. and 760 mm., or 95 B.Th.U. per cu. ft. (or about 840 kg.-cal. per cu. metre) at 15° and 760 mm. It burns with a feebly luminous greenish-blue flame, and requires 0·7 of its own volume of air for theoretically complete combustion resulting in products containing 25% of carbon dioxide.

It leaves the furnace heavily charged with dust; and although the coarser and heavier particles are deposited in "dust-catchers" inserted in the down-coming gas-main from the furnace, as well as in the gas-flues leading therefrom, there still remains about 5 g. per cu. m. or nearly 0·3 lb. per 1,000 cu. ft. of fine dust. A Cleveland furnace with an output of 1,000 tons of pig-iron per week will produce about 1,113,000 cu. ft. of such gas per hour with a potential heat content of some 1,113 therms, and a sensible heat (assuming a temperature of 250°C.) of 88·6 therms. Leaving the sensible heat out of consideration, the potential heat in the gas if burned in a gas-engine working at 25% efficiency, would be capable of developing continuously no less than 10,850 brake horsepower. This very large supply of energy is utilised in three ways, (i) to pre-heat the blast, (ii) to generate the power necessary to produce the blast and to work the hoists, and (iii) for other purposes such as the generation of electricity or, mixed with coke-oven gas, for firing re-heating furnaces and the like. Whether it is to be used for production of power or for the firing of hot-blast stoves, it is advantageous that the gas should be cleaned to reduce the dust-content. Suitable limits are between 0·3 and 0·5 g. of dust per cu. m. if the gas is to be employed for firing boilers or for heating the hot-blast stoves, and 0·01 g. per cu. m. prior to use in gas-engines. The average efficiency of utilisation of uncleaned blast-furnace gas when burned under Lancashire boilers was, according to observations since 1914, not over 60% even under the most favourable conditions, whereas in recent practice cleaned gas when burned under water-tube boilers has enabled efficiencies exceeding 80% to be realised. Similarly, the efficiency of hot-blast stoves has been raised from about 66 to 83%.

Preliminary cleaning of the gas to a dust content of from 0·3 to 0·5 g. per cu. m. has been accomplished by electrostatic cleaners of the Lodge-Cottrell type, very little loss of sensible heat taking place, the cost being given as about 0·028*d.* per 1,000 cu. ft. Before the gas can be used in gas-engines, however, further cleaning is necessary, successful results being obtained by filtering it as in the Halberg-Beth plant which is illustrated in Fig. 11. The slightly warm gas is filtered through bags made of a special fabric, arranged 12 in a compartment with a mechanism for periodic shaking, whereby its dust content

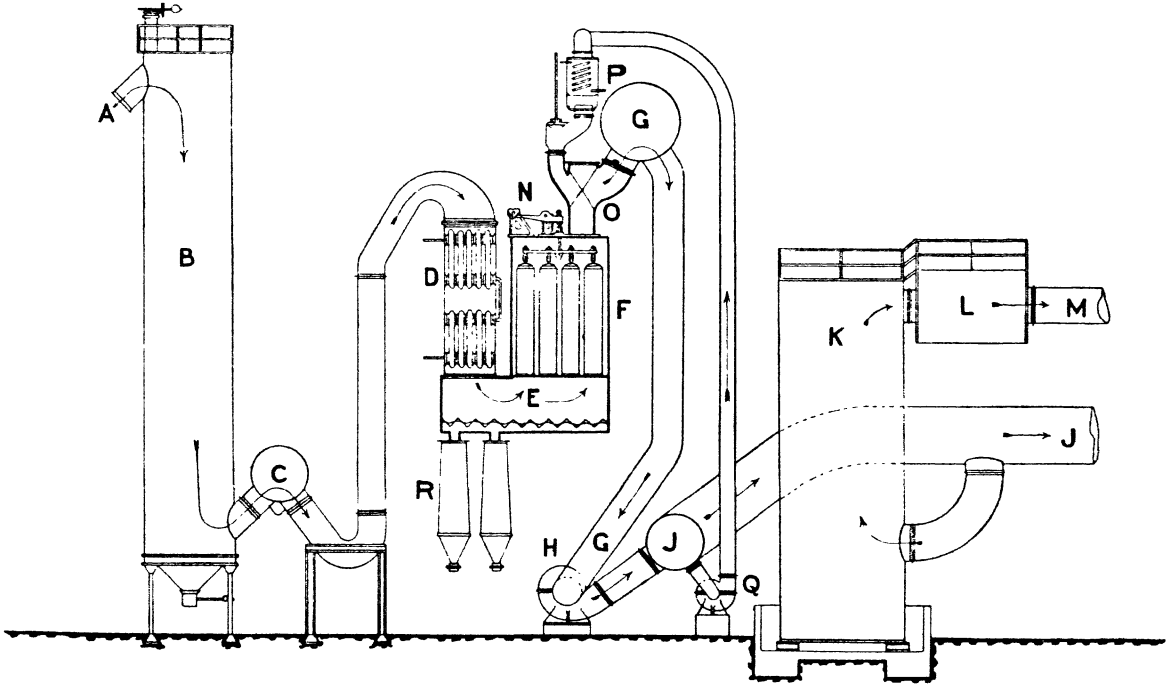


FIG. 11.—THE HALBERG-BETH SYSTEM OF DRY GAS-CLEANING.

A. Gas inlet from furnace dust catcher.
B. Pre-cooler.
C. Cooled gas collecting main.
D. Pre-heater.
E. Dust chamber with screw conveyor.
F. Filter compartment with bags.
G. Clean gas suction mains.
H. Main fan.
J. Clean gas delivery main for heating supply.
K. Final cooler for gas-engine supply.
L. Final dryer for gas-engine supply.
M. Delivery main for gas-engine supply.
N. Shaking gear for cleaning bags.
O. Change-over valve for counterblast (Reversed gas current for cleaning bags).
P. Reheater for counterblast.
Q. Small fan for counterblast.
R. Dust hoppers.

may be reduced to below 0·005 g. per cu. m. One such cleaning plant at Frodingham in Lincolnshire, with a total rated capacity of 4 million cu. ft. per hour, reduces the dust content of 3 million cu. ft. of gas per hour down from 6 g. to between 0·003 and 0·005 g. per cu. m.

The operating costs of cleaning the gas to a dust content below 0·05 g. per cu. m. by the foregoing methods are said to be of the order of 0·06*d.* to 0·10*d.* per 1,000 cu. ft.

Blast-furnace gas, when cleaned to the degree already mentioned, is eminently suitable for use in large gas-engines, and modern engines of from 2,000 to 5,000 H.P. when coupled to electric generators have an over-all efficiency of not less than 25% at the switchboard and are widely used for the purpose. Further economy is possible by recovering part of the waste heat in the gas-engine exhaust in waste-heat boilers which may be advantageously fed with the hot water leaving the cylinder-jackets of the engine. Gas which is in excess of that required to heat the blast and for power-generation is frequently mixed with coke-oven gas to give a mixed gas the calorific value of which is about 105 B.Th.U. per cu. ft., the mixture being used for firing open-hearth steel-furnaces and the like. The maximum economy, however, can only be effected in self-contained works in which coke-ovens, blast-furnaces and steel works are concentrated on the same site. For a more detailed development of this subject, *see* W. A. Bone and G. W. Himus, "Coal, Its Constitution and Uses," 1936.

Liquid Fuels from Coal.—Liquid fuels may be derived from coal in several ways as indicated in the scheme on p. 360.

(1) By carbonisation at high or low temperatures, between 2 and 3 gallons per ton of low-boiling spirit suitable for use in spark-ignition internal combustion engines are obtainable by fractionating the tars and scrubbing the gases; the low temperature tar is suitable for use as fuel oil although its calorific value is appreciably lower than that of fuel oil derived from petroleum (some 9,000 kg.-cal. per kg. as compared with over 10,000). On the other hand, low temperature tar may be hydrogenated to give about 80% by volume of motor spirit and 20% by volume of Diesel oil.

(2) By hydrogenation; this subject will be treated under "Hydrogenation of Coal."

(3) An alternative method of producing liquid fuels from coal which is attracting a good deal of attention is that known as the "Fischer-Tropsch" process which operates at atmospheric pressure. The process consists in synthesising aliphatic hydrocarbons from water-gas or a gaseous mixture containing carbon monoxide and hydrogen in the ratio of 1/2. Such a mixture may be obtained by blowing a water-gas generator with 10 cu. ft. of coke-oven gas per lb. of steam which gives a gas containing H_2 60, **CO** 30, N_2 and other gases 10%; 330 cu. ft. of coke-oven gas and 12 lb. of steam are used for every 1,000 cu. ft. of gas produced. The gas must be purified from dust, H_2S and finally from organic sulphur, which should not exceed 0·2 g. per 100 cu. m. (0·087 grains per cu. ft.). The gas is passed through a reaction chamber containing an appropriate catalyst. The most effective catalysts belong to the 8th group and contain either **Ni** or **Co**. The catalysts diminish in activity owing to impregnation by waxes which must be periodically removed by solvents. Successful operation depends *mainly* on the catalyst and maintenance of uniform temperature (about 200°C.) during the exothermic reaction, some 600 kg.-cal. per cu. m. (67·3 B.Th.U. per cu. ft.), or 20% of the potential heat of the gas being liberated. The catalysts employed by the Ruhr-Chemie A.-G. are said to require re-activation at the end of 3 months and are made by precipitating such materials as **Ni-Th, Ni-Mn-Al** or **Co-Th** on infusorial earth.

Theoretically, about 1·4 gallons of oils (sp.gr. 0·76) should be yielded by 1,000 cu. ft. of gas; the highest yield reported is 72%. Typical products are as follows:

	B.pt. °C.	Weight, %.	Olefines, %.
Low boiling fraction	<30	4	50
"*Kogasin I*" (motor spirit) .	30–200	62	30
"*Kogasin II*" (motor spirit) .	>200	23	10
Hard and soft waxes . . .	—	11	—

The principal fraction, Kogasin I, consists mainly of paraffins and hence has a low octane number, but by treatment with 0·8 ml. lead tetraethyl per litre the octane number may be raised to 78 which is that of "Ethyl" spirit. The heavier oil, by reason of its high paraffin content, is ideal for Diesel engines. It is reported that lubricating oils are obtainable from the highest-boiling and intermediate fractions by suitable treatment. A Fischer plant to make 25,000 tons of petrol per annum was started in April, 1936, for the Braunkohle-Benzin A.-G. at Brabag, Ruhrland, and is to be extended to make 150,000 tons per annum, brown coal briquettes being used in the producers, while the Rheinpreussen Co. at Homberg (Rhineland) are to make 30,000 tons of petrol per annum from a mixture of coke water-gas and coke-oven gas. Further information on the subjects dealt with in this section may be obtained from papers by K. Gordon (J. Inst. Fuel, 1935) and F. Fischer (*ibid.* 1936).

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B. Petroleum and Shale Oil.

It has already been shown on p. 331*c* that in 1935 the fuel requirements of the world included some 235 million metric tons of crude petroleum (to which also should be added a relatively small proportion—probably not exceeding a million tons— of shale oil), or approximately 15% by weight. The calorific value of petroleum, however, is such that between 25 and 30% of the total fuel-energy requirements of the world were supplied by petroleum. There are certain purposes (*e.g.* for automobile and aero-engines) for which volatile hydrocarbon oils are employed without displacing coal, while in other directions (especially in marine propulsion), there has been direct replacement of coal by oil, all the navies and much of the mercantile marine of the world using oil, either for steam-raising or else in internal combustion engines. The advantages of oil for marine work include: (i) high thermal-storage value leading to economy of space; (ii) ease and rapidity in bunkering; (iii) flexibility, giving ready and immediate response to varying loads; (iv) possibility of forcing boilers to extreme duties in case of emergency; (v) absence of smoke under normal working conditions, coupled with ability to produce smoke screens in case of need; (vi) abolition of stoking; and (vii) ability to secure and maintain higher speeds than would be possible with coal firing. Some of these advantages are also of value in relation to locomotive-boiler firing, especially in countries (United States, Russia) where petroleum is abundant. In the Report issued by the U.S. "Liquid Fuel" Board in 1904, the relative all-round efficiencies of oil and good steaming-coal, from the naval point of view, are estimated to be as 18/10, whilst Mr. James Holden, locomotive superintendent of the Great Eastern Railway, in giving evidence before the Royal Commission on Coal Supplies (1905), stated that, according to his experience, petroleum fuel oil had, weight for weight, approximately twice the steam-raising power of coal in locomotive boilers. The latter estimate is probably based on the best rather than on the average results obtained with oil fuel, but certainly the ratio is not less than 3/2. Moreover, weight for weight, oil occupies much less space than coal, and further, oil does not deteriorate on long keeping as does coal.

The world production of shale oil is relatively of very little importance. In 1932, which is the last year for which complete returns are available, 3·8 million metric tons of oil shale were produced, Manchuria and Scotland each supplying about 1·4 million tons; from 1·41 million Imperial tons raised in Scotland in 1936, 30½ million gallons of crude oil and crude naphtha were obtained, so that the shale-oil output from 3·8 million metric tons would probably be between 50 and 100 million gallons, or, say, from 1½ to 3 million barrels. The products from Scottish shale oil are: naphthas 10, burning oils 16, wax 9, heavy fuel oil 54, loss 11%. The calorific value of the fuel oil ranges from 10,900 to 11,100 kg.-cal. per kg.

In applying oil to boiler and furnace work generally, the fuel must be "atomised" and delivered into the combustion chamber in the form of a fine spray in order to secure intimate mixing with the air required for combustion. Atomisation may be brought about in three ways, (i) by steam, (ii) by air at high- or low-pressure, and (iii) by mechanical means, the oil being forced through a suitable orifice under pressure. The relative advantages of the three systems may be summarised as follows: Steam atomisation is particularly convenient for oil-fired boilers and in plant where a supply of dry steam is constantly available, moreover where oils of high viscosity are to be burned, the oil is preheated by the steam used for atomisation. Air-atomisation has the obvious advantage that the atomising material is usefully employed in the subsequent combustion and stack losses are not (as with steam) augmented by the atomising agent; generally speaking, low-pressure air (about 8 oz. per sq. in.) is preferable to air at higher pressures since not only is it cheaper but, in addition, a higher proportion of the total air required for combustion is delivered with the oil into the furnace; mechanical atomisation requires no steam or air lines in addition to the oil-supply pipe and less energy is required for atomisation than with steam or air: on the other hand, the plant is more costly owing to the extra strength of pipes and pumps which is necessary, the plant is less flexible in respect of varying load since the quantity of oil passed by a given orifice does not vary greatly with change of oil-pressure.

In addition to fine atomisation of the fuel and its intimate mixture with the air required for combustion, it is necessary that the furnace volume should be ample in order that combustion may be completed before the products come into contact with relatively cool metallic surfaces, otherwise serious loss of heat will arise from the escape of incompletely burned gases and vapours. Oil requires per unit of weight from 25–30% more air for complete combustion than coal, and in addition *all* the combustion of oil takes place in the free combustion space of the furnace, whereas with coal approximately half of the combustion occurs on the grate and only half in the combustion space. For further details as to liquid fuels generally, *see* J. S. S. Brame and J. G. King, "Fuel," E. Arnold, 1935; R. T. Haslam and R. P. Russell, "Fuels and Their Combustion," McGraw-Hill Book Co., 1926; and "The Science of Petroleum," Oxford University Press. 1938.

G. W. H.

FUEL OIL (*see above* and Vol. III, 423*d*).

FUKUGETIN *v.* Fukugi.

FUKUGENETIN, *iso*FUKUGENETIN *v.* Fukugi.

FUKUGI. The Japanese dyestuff "fukugi," obtained from the bark of the *Garcinia spicata* or *Xanthocymus ovalifolius*, has been employed to a considerable extent as a mordant dyestuff in Japan. The extract of the bark is sold in the form of brittle rectangular cakes of a yellowish-brown colour.

A. G. Perkin and Phipps (J.C.S. 1904, **85**, 56) isolated a colouring matter, *fukugetin*, minute canary-yellow prismatic needles, m.p. 288–290°, to which they assigned the formula $C_{17}H_{12}O_6$. (now believed to be $C_{24}H_{16}O_9$, *v. infra*). It dissolves in alkaline solutions with a yellow colour and gives with lead acetate an orange-yellow precipitate. By fusion with alkali, phloroglucinol and protocatechuic acid are obtained. The *bromine compound* forms minute flat needles, m.p. 280°.

Fukugetin has similar dyeing properties to luteolin, and also resembles this colouring matter in that its alkaline solution is not oxidised on exposure to air.

In addition to fukugetin, Shinoda (J. Pharm. Soc. Japan, 1926, No. 535, 69; 1927, No. 541, 35; 1932, **52**, 167) obtained a second colouring matter, *garcinin*, $C_{16}H_{12}O_6$ or $C_{16}H_{10}O_6$, or $C_{28}H_{20}O_{10}$ (now believed to be $C_{15}H_{10}O_5$, *v. infra*), which decomposes at 254° and differs from fukugetin mainly in its solubility in alcohol. The colour reactions of the two substances with sulphuric acid are similar, and both yield, on reduction with magnesium and hydrochloric acid, a purple colour indicating the presence of the γ-pyrone nucleus. When fused with alkali, garcinin, like fukugetin, gives phloroglucinol and protocatechuic acid.

The following derivatives of fukugetin are described: *diacetyl*, m.p. 252–254°; *triacetyl*, m.p. 272–273°; and *tetra-acetyl*, m.p. 160°; the tetra-acetyl compound is probably identical with the triacetyl derivative, m.p. 160°, of Maniwa (Chiba Yakugaku Si, 1924, No. 2).

Fukugetin hexamethyl ether, m.p. 202–204°, is converted by treatment with alcoholic potassium hydroxide into a phenolic *substance*, m.p. 202°, a yellow *compound*, m.p. 227–228°, which gives with magnesium and hydrochloric acid a red coloration, veratric acid and an *acid*, m.p. 215–216°, giving a violet coloration with ferric chloride.

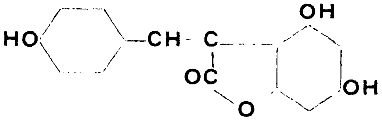
When decomposed by 50% potassium hydroxide in an atmosphere of hydrogen, fukugetin yields acetic acid, *anhydrofukugetin*, $C_{19}H_{12}O_6$, m.p. above 300°, *fukugenetin*, $C_{19}H_{14}O_7$, m.p. 205°, phloroglucinol and *garcinol*, yellow needles, m.p. 308°.

Acetylation of anhydrofukugetin gives *acetylfukugenetin*, m.p. 265°, whilst methylation and ethylation yield *methylfukugenetin*, m.p. 204°, and *ethylfukugenetin*, m.p. 171–172°, respectively.

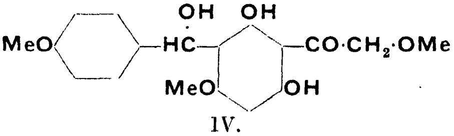
Fukugenetin or anhydrofukugetin are converted by treatment with 50% potassium hydroxide into acetic acid, 3:4-dihydroxyacetophenone, garcinol and an *acid*, m.p. 198°.

According to Shinoda and Ueda (J- Pharm. Soc. Japan, **1933**, **53**, 167), garcinol contains three phenolic hydroxyl groups, a double bond and a lactone ring. The *triacetyl* derivative, m.p. 202°; *tribenzoyl* compound, m.p. 224°; *trimethyl ether*, m.p. 168·5°; *dihydro*-derivative, m.p. 242–243°; and *dihydrotrimethyl ether*, m.p. 95°, are described. By fusion with alkali, phloroglucinol and an *acid*, m.p. 182°, are formed, whilst oxidation of the trimethyl ether gives anisic acid, and the authors assign the formula $C_{16}H_{12}O_5$ to garcinol and suggest structural formulæ for garcinol and fukugetin.

On the other hand, Murakami and Irie (Proc. Imp. Acad. Tokyo, 1934, **10**, 568) show that garcinol, obtained together with fukugenetin and 3:4-dihydroxyacetophenone by treating fukugetin with 50% potassium hydroxide solution, has the formula $C_{15}H_{10}O_5$, and readily yields a dihydro-derivative by catalytic reduction. When treated with methyl sulphate and potassium hydroxide, it is converted, by opening of the lactone ring, into *pentamethylgarcinol hydrate*, m.p. 142–143°, which was proved by synthesis to be the methyl ester of α-carboxy-2:4:6:4′-tetramethoxystilbene. Garcinol is, therefore, 2-*p*-hydroxybenzylidene-4:6-*iso*coumarone:



Fukugetin and garcinin are considered by Murakami (*ibid.* 1932, **8**, 500) to be isomers of the formula $C_{22}H_{16}O_8$. With methyl sulphate, these substances give crystalline *pentamethyl ethers*, decomposing at 141–143°, both of which contain three hydroxyl groups (Zerevitinov), and with boiling alcoholic potassium hydroxide yield veratric acid, a little anisic acid and a *phenol*, $C_{15}H_8O(OH)_3(OCH_3)_3$, to which



IV.

formula (IV) is assigned.

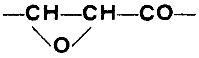
Shinoda and Ueda (*l.c.*), however, suggest that garcinin is a monoacetyl derivative of fukugetin, whilst Murakami and Irie (*l.c.*) finally conclude that it is impure fukugetin.

The composition of fukugetin is stated by Murakami and Irie (*l.c.*) to be $C_{24}H_{16}O_9$ instead of $C_{22}H_{16}O_8$ as previously suggested. By acetylation with acetic anhydride and sodium acetate, *tetra-acetylanhydrofukugetin*,

$$C_{24}H_{10}O_4(O{\cdot}COMe)_4,$$

m.p. 273–274°, is obtained, whereas methylation with methyl sulphate yields *anhydrofukugetin tetramethyl ether*, m.p. 252–254°.

With diazomethane, fukugetin gives the *pentamethyl ether*, m.p. 202°, which is rapidly converted by hot 5% alcoholic potash into *iso-fukugetin pentamethyl ether*, m.p. 136°, previously described as fukugetin pentamethyl ether. The *iso*-derivative yields with methyl sulphate *iso-fukugetin hexamethyl ether*, m.p. 188°, which is stable to potassium hydroxide solution, but is transformed into fukugetin pentamethyl ether by hydrochloric acid. The isomerisation of fukugetin pentamethyl ether to its *iso*-derivative is due to the change of the group :



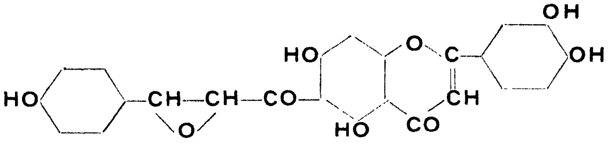
$$\text{—CH—CH—CO—}\ (\text{bridged by }\text{O})$$

(formula V)

to

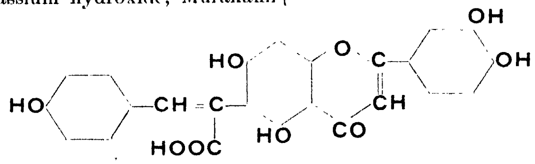
$$\text{--CH=C(OH)—CO—}$$

Since fukugetin is soluble in potassium hydroxide solution and is precipitated therefrom by carbon dioxide, it does not contain a carboxyl group or lactone ring, and the following structural formula is assigned to this colouring matter:



V.

Fukugenetin and iso*Fukugenetin*.—By heating fukugetin with 50% potassium hydroxide solution in an atmosphere of hydrogen, Shinoda (*l.c.*) isolated, amongst other products, fukugenetin, an isomer of fukugetin. Employing 30% aqueous potassium hydroxide, Murakami and Irie (Bull Chem. Soc. Japan, 1936, **11**, 288) obtained a mixture of two substances, fukugenetin and iso*fukugenetin*, m.p. above 380°; these are considered to be *cis-trans* isomers of the formula :



Fukugenetin and *iso*fukugenetin could not be separated directly, but by methylating the mixture with methyl sulphate the *hexamethyl* derivatives, m.p. 208 and 199-200°, respectively, were produced, and these were separated by fractionation from alcohol. The presence of a carboxyl group in *iso*fukugenetin was proved by boiling hexamethyl*iso*fukugenetin with 10% potassium hydroxide solution, by which means an *acid*, $C_{28}H_{24}O_9$, m.p. 258–260°, was produced.

Treatment of the mixture of the two isomers with alcoholic sulphuric acid gives fukugenetin, which is unaffected, and *anhydro*iso*fukugenetin*, $C_{24}H_{14}O_8$, m.p. above 380°; the latter is reconverted into *iso*fukugenetin by hydrolysis with 10% potassium hydroxide solution at room temperature. During the formation of anhydro*iso*fukugenetin one active hydrogen is lost since only a *triacetyl* derivative, m.p. 267°, is obtained by acetylation with acetic anhydride and sodium acetate.

Methylation of anhydro*iso*fukugenetin yields *pentamethyl*iso*fukugenetin*, m.p.178·5–179°, which contains one active hydrogen and is converted into the hexamethyl derivative by further methylation.

Dyeing Properties.—According to Perkin and Phipps (*l.c.*), fukugetin yields the following shades on mordanted fabrics :

Chromium.	Aluminium.	Tin.	Iron.
Dull orange-yellow.	Orange-yellow.	Bright yellow.	Olive-brown.

The dyeing properties of fukugi are analogous to those of weld. The similarity in shade, indeed, is so marked that, except in point of strength—for fukugi is a stronger dye than weld—it is impossible to distinguish between them.

A. G. P. and E. J. C.

FULLER'S EARTH. (Fr. *Terre à foulon*, Ger. *Walkerde*.) A term applied to a variety of clay-like materials which possess in common the property of adsorbing grease and oil, and hence are used by fullers for cleansing woollen goods. They vary in colour with dull shades of grey, yellowish, bluish or greenish, and are soft, with an earthy appearance. They are greasy and unctuous to the touch, and do not adhere to the tongue. When a lump of the dried earth is placed in water, it presents a very curious appearance as it crumbles down to a fine powder; and is not plastic like ordinary clays. Mineralogically they appear to be mixtures; few approximate to kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) in composition, and many may be referred to the "smectite" of A. Breithaupt (1841), a greenish-grey clay from Cilly in Styria. Optical and X-ray data (P. F. Kerr, 1932–37) indicate that montmorillonite is an important constituent and A. Brammall and J. G. C. Leech (Geol. Mag. 1940, **77**, 102) conclude that montmorillonite is the main constituent (76–90%) of Nutfield fuller's earth. The chemical composition varies widely, and is no guide to the commercial value of the material, which depends rather on the physical state of aggregation. Sp.gr. 1·75–2·5; *n* 1·485–1·532. Plots of analyses of clay minerals of the fuller's earth group show a range in the ratio $SiO_2{:}Al_2O_3$ from 4·5 to 9 (S. I. Tomkeieff, Min. Mag. 1933, **23**, 463). A suggested formula is

$$x[9SiO_2{\cdot}6(Mg,Fe'',Ca)O{\cdot}12H_2O]+ y[9SiO_2{\cdot}2(Al,Fe''')_2O_3{\cdot}12H_2O]$$

(J. de Lapparent, Compt. rend. 1935, **201**, 481).

The following analyses are of: I, smectite from Cilly, Styria (P. F. Kerr, Amer. Min. 1932, **17**, 196); II, bluish-grey fuller's earth from Nutfield, Surrey (P. G. Sanford, Geol. Mag.

1889, 456, 526), on material dried at 100° with a loss of 27·47% water; 13·33% of all the solid constituents, except silica, are soluble in acid; III, yellowish fuller's earth from Nutfield, Surrey (P. G. Sanford, 1889), on material dried at 100° with loss of 29·56% water; 10·73% solids, soluble in acid; IV, from Attapulgus, Georgia, U.S.A. (P. F. Kerr, Amer. Min. 1937, **22**, 543); V, from Martvili, Georgia, U.S.S.R. (A. A. Tvaldchrelidze, Bull. Univ. Tiflis, 1923, **3**, 334; Mineralogical Abstracts, 1926, **3**, 68); VI, from Tehachapi, California (P. F. Kerr and E. N. Cameron, Amer. Min. 1936, **21**, 235). Later analyses and base-exchange data by Brammall and Leech (*l.c.*).

	I.	II.	III.	IV.	V.	VI.
SiO_2	52·43	62·81	59·37	53·42	49·22	53·88
TiO_2	0·08	--	-	0·52	--	0·44
Al_2O_3	15·95	6·92	11·82	10·06	16·61	11·66
Fe_2O_3	1·42	3·78	6·27	3·40	2·46	4·60
FeO	0·10	—	-	0·18	0·44	
MnO	—	—	—	0·02	--	0·18
MgO	5·02	2·27	2·09	9·16	4·22	8·61
CaO	2·97	7·40	6·17	1·29	3·77	1·56
Na_2O	—	-	-	0·02		0·15
K_2O	-	0·74	0·84	0·64	--	0·39
P_2O_5	0·08	0·27	0·14	0·12	-	0·16
SO_3	0·22	0·05	0·07	0·04	-	nil
H_2O+	7·60	15·57	13·19	9·42	6·46	9·98
H_2O-	13·96	-	—	11·83	16·12	8·21
	100·13	99·86	100·10	"99·96"	99·40	99·82

I, also C 0·30; II, also NaCl 0·05; III, also NaCl 0·14; IV, also CO_2 0·10, Cl 0·02.

Fuller's earth occurs as beds in sedimentary rocks belonging to various geological periods, ranging from the Silurian to the Eocene. The most important deposit in England is a bed 8–12 ft. in thickness, lying between sandstones in the Lower Greensand division of the Cretaceous system. This is worked in open pits at Nutfield and Redhill in Surrey. Nearer the surface, where oxidised, it is yellowish, but lower down it is bluish in colour. In Somersetshire, Gloucestershire and Dorsetshire, the "fuller's earth formation" of geologists, lying between the limestones of the Great Oolite and the Inferior Oolite, consists of a thick deposit of clays and marls, with beds 2–3 ft. in thickness of fuller's earth of good quality. This was formerly extensively worked for use in the cloth mills of the west of England, but now is obtained only on the Downs to the south of Bath. Still smaller quantities were formerly yielded by the Lower Greensand strata near Woburn in Bedfordshire. On the petrography of English fuller's earth, *see* E. F. Newton, Proc. Geol. Assoc. 1937, **48**, 175.

For many years the English fuller's earth was considered the best, and until recently large quantities were exported to America. Deposits have now been opened up at several places in the United States, chiefly in Florida, and to a lesser extent in Georgia, Alabama, Arkansas and California. In Gadsden Co., Florida, it occurs as a bed 4–12 ft. in thickness in bedded clays and sandy clays of Oligocene (Tertiary) age. American and Caucasian occurrences are often associated with volcanic rocks, and it is suggested that, together with bentonite, the material has originated by the decomposition of a glassy volcanic ash. Small outputs are also recorded from India and Australia (Wingen, New South Wales).

The English output amounts to about 15,000 tons per annum, whilst double this quantity is now obtained in America. The price at the pits ranges from 25*s*. to £2 per ton. The earth as dug is dried, crushed and passed through fine sieves of silk or bronze gauze.

Although still used for cleaning cloths, scouring yarns and washing woollens and fine-dyed goods, fuller's earth now finds a more extensive use in the refining of oils, grease and lard. Mineral oils are decolorised and clarified by allowing the oil to percolate through long cylinders filled with coarser fuller's earth. Vegetable oils, such as cotton-seed oil, are warmed, stirred with 5–10% earth and filtered through bags. The main points to be determined in the valuation of the earth in the oil industry are the relative bleaching power and the quantity of oil absorbed. For a method of testing fuller's earth for these factors, *see* Richert, Ind. Eng. Chem. 1917, **9**, 599; Analyst, 1917, **42**, 340. Fuller's earth has also been used in the manufacture of pigments for printing wall-papers. Small quantities of the finest grades are used for toilet preparations.

References.—J. T. Porter, 'Properties and Tests of Fuller's Earth, U.S. Geol. Survey, Bull. 315, 1907; H. Ries, "Clays, their Occurrence, Properties, and Uses," 3rd ed., New York, 1927; C. L. Parsons, U.S. Bureau of Mines, Bull. 71, 1913. "Fuller's Earth," Imp. Min. Res. Bur. London, 1920.

L. J. S.

FULLER'S EARTHS (*v.* Vol. IV, 247).

"*FULLPULVER*" —02 (*v.* Vol. IV, 467*a*).

FULMINATES (*v.* IV, 535*d*).

FULMINIC ACID (Ger. *Knallsäure*)

C:NOH.

The acid has not been obtained in a free state. Scholvien (J. pr. Chem. 1885, [ii], **32**, 461) obtained an ethereal solution of the acid by treating sodium fulminate with dilute sulphuric acid, keeping the mixture cool and dissolving the yellow oil thus obtained in ether. Wieland and Hess (Ber. 1909, **42**, 1346) have confirmed this statement, and found that the acid rapidly polymerised to metafulminuric acid (*v. infra*). Howard first showed that when silver nitrate or mercuric nitrate was treated with alcohol and excess of nitric acid, a crystalline, detonating precipitate, fulminating silver or fulminating mercury, was obtained. Analyses of these substances (Liebig, Ann. Chim. Phys. 1823, [ii], **24**, 312; Annalen, 1838, **27**, 133; Liebig and Gay-Lussac, Ann. Chim. Phys. 1824, [ii], **25**, 285; Divers and Kawakita, J.C.S. 1884, **45**, 17) show that they are salts of an acid possessing the formula **HCNO**. The constitution of this acid has given rise to much discussion. Berzelius wrote fulminating silver as

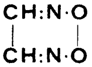
$$Ag_2O\cdot(AgN)_2\cdot C_4N_2O_3.$$

This formula accounted for the fact that in many of its reactions only half of the metal is separated, also that the double fulminate of potassium and silver detonates as violently as fulminating silver itself, the detonation being attributed to the decomposition of the group **AgN**. Laurent and Gerhardt next proposed the constitution $C_2N(NO_2)Ag_2$, assigning the explosive nature of the body to the presence of a nitro group, and the subsequent experiments of Kekulé (Annalen, 1857, **101**, 200; 1858, **105**, 279) and Schischkoff (*ibid.* **101**, 213) apparently confirmed this view.

Later Kekulé formulated fulminic acid as nitroacetonitrile, $CH_2(NO_2)CN$. He based this formula chiefly on two reactions which fulminic acid undergoes. When mercuric fulminate is treated with sulphuretted hydrogen, ammonium thiocyanate is produced, and with aqueous hydrochloric acid, hydroxylamine is the main product. The production of ammonium thiocyanate suggests that in fulminic acid there is a (**CN**) group, and that the two nitrogen atoms are in different states of combination, which facts fit in with the formula proposed. But of the two nitrogen atoms only one is represented as oxidised and capable of conversion into hydroxylamine, whereas Divers and Kawakita (J.C.S. 1884, **45**, 16) have shown that both atoms of nitrogen are so convertible. Schischkoff (Bull. Soc. chim. 1860, [ii], **2**, 294) doubted Kekulé's formula. Steiner proposed

$$HO\cdot N:C:C:N\cdot OH$$

as the correct configuration (Ber. 1876, **9**, 779); and Scholl formulated fulminic acid as glyoxime peroxide



$$\begin{array}{l} CH:N\cdot O \\ \vert \qquad \vert \\ CH:N\cdot O \end{array}$$

In 1894 Nef found that on treating sodium nitromethane with mercuric chloride, mercuric fulminate was produced, and, moreover, that sodium nitromethane, on treatment with aqueous hydrochloric acid, decomposed into formic acid and hydroxylamine, as does fulminic acid (*v. supra*). On these grounds Nef formulated fulminic acid as carbonyl monoxime, **C:NOH**, and represented the production of mercuric fulminate from nitromethane as follows:

$$CH_3NO_2 \xrightarrow{\text{Alkali}} CH_2:NO\cdot ONa$$

Pseudo-modification.

$$\xrightarrow{HgCl_2} (CH_2:NO\cdot O)_2Hg$$

Unstable.

$$\xrightarrow{-H_2O} (C:NO)_2Hg$$

The explosive character of the fulminates is accounted for by the presence of bivalent carbon in the molecule. It was an old observation, first recorded by Liebig, that when mercuric fulminate was treated with hydrochloric acid of a certain strength, prussic acid was evolved, and this fact was long used to support the nitroacetonitrile formula for fulminic acid. But Nef showed that the compound formed was not prussic acid, but chloroformaldoxime, a compound possessing an odour similar to that of prussic acid.

$$C:NONa + 2HCl = CHCl:NOH + NaCl$$

Hydrochloric acid converts chloroformaldoxime into hydroxylamine hydrochloride; sodium hydroxide regenerates a fulminate (Nef, Annalen, 1894, **280**, 263, 305). Moreover, nitroacetonitrile has been prepared by removing the elements of water from methazonic acid, $C_2H_4O_2N_2$, and is found to have none of the characteristic properties of fulminic acid (Steinkopf and Bohrmann, J. pr. Chem. 1910, [ii], **81**, 97, 193; Ber. 1908, **41**, 1044). Scholl (*ibid.* 1899, **32**, 3492) applied Friedel and Craft's reaction to fulminic acid, and found that on gently warming mercuric fulminate with benzene, aluminium and aluminium chloride, benzaldoxime is produced, a further confirmation of Nef's carbonyloxime formula. Angelico (Chem. Zentr. 1901, II, 404) obtained fulminic acid by treating a solution of mercuric nitrate in excess of dilute nitric acid with a concentrated solution of malonic acid and a few drops of sodium nitrite solution. The course of the reaction is as follows:

$$CH_2(COOH)_2 \rightarrow C:NOH(COOH)_2$$

*iso*Nitrosomalonic acid.

$$\rightarrow C(:NOOH)(COOH)_2$$

*iso*Nitromalonic acid.

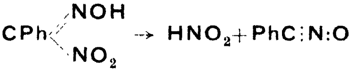
$$\rightarrow CH(:NOOH)COOH$$

*iso*Nitroacetic acid.

$$\rightarrow CH_2:NOOH \rightarrow C:NOH$$

*iso*Nitromethane.

Wieland and Semper (Ber. 1906, **39**, 2522) have shown that phenylmethylnitrolic acid readily decomposes into nitrous acid and the unstable benzonitrile oxide.



$$CPh\begin{matrix} \diagup NOH \\ \diagdown NO_2 \end{matrix} \rightarrow HNO_2 + PhC \vdots N:O$$

Hence, if a similar decomposition occurs in the case of methyl nitrolic acid, the hitherto unknown nitrile oxide $H\cdot C \vdots N:O$ or the products of its decomposition would be obtained. Wieland (*l.c.*) has shown that the products of the decomposition of methylnitrolic acid are fulminic acid, formic acid and hydroxylamine, the decomposition being analogous to that of chloroformaldoxime. The unstable nitrile oxide is probably formed first and then undergoes an isomeric change into fulminic acid.

Wöhler (*ibid.* 1905, **38**, 1351) has determined the molecular weight of fulminic acid by means of the sodium salt, which can be prepared in a pure anhydrous state by the action of sodium amalgam on mercury fulminate suspended in alcohol. The numbers obtained by the cryoscopic method and by determining the equivalent conductivities of dilute solutions correspond closely with the numbers required for the monomolecular formula **C:NONa**.

In the ordinary method of preparing fulminates by the oxidation of ethyl alcohol, the following changes are supposed to occur (Wieland, Ber. 1907, **40**, 418):

$$CH_3\cdot CH_2\cdot OH \rightarrow CH_3\cdot CHO$$

Aldehyde.

$$\rightarrow CH(:NOH)\cdot CHO$$

*iso*Nitrosoacetaldehyde.

$$\rightarrow CH(:NOH)\cdot COOH$$

*iso*Nitrosoacetic acid.

$$\rightarrow NO_2\cdot C(:NOH)\cdot COOH$$

*iso*Nitrosonitroacetic acid.

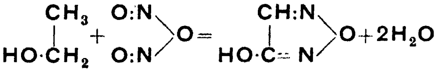
$$\rightarrow NO_2\cdot CH:NOH \rightarrow C:NOH$$

Methylnitrolic acid.

The experimental evidence in favour of the above hypothesis is as follows: Wöhler and Theodorovits (Ber. 1905, **38**, 1345) found paraldehyde to be a more suitable agent than alcohol for the preparation of fulminates, and the formation of methylnitrolic acid from *iso*nitrosoacetic acid has been accomplished by Ponzio (J.C.S. 1903, **84**, I, 453), Wieland has prepared mercuric fulminate from methylnitrolic acid (*v. supra*); and lastly by treating fulminic acid with nitrous acid, Palazzo (*ibid.* 1907, **90**, I, 489) has obtained methylnitrolic acid as one of the products of the reaction.

The older view of Kekulé as to the constitution of fulminic acid has now been finally abandoned, and the carbonyloxime formula of Nef has taken its place.

Hodgkinson (J.S.C.I. 1918, **37**, T190 has pointed out that mercury fulminate cannot be formed in the absence of nitrous acid or a mixture of nitric oxide and nitrogen peroxide; he, therefore, represents the formation and constitution of fulminic acid by the equation:



Halogen derivatives.—The addition of halogens to free fulminic acid prepared *in situ* affords the following additive products in good yields: $CCl_2:NOH$, b.p. 45°/12 mm.;

$$CBr_2:NOH,H_2O,$$

m.p. 40°; $CBr_2:NOH$, m.p. 68–9° (Me ester by CH_2N_2. b.p. 139–141°); $CI_2:NOH,H_2O$, m.p. 52°; $CI_2:NOH$, m.p. 69°; the chloro-compounds are the most and the iodo-compounds the least stable. The initial products of the decomposition by heat of these substances (130°, 80° and room temperature respectively) are the halogenocyanogens and hypohalous acids.

Mercuric fulminate or **fulminating mercury** (*v.* Vol. IV. 536).

Silver fulminate, *Fulminating silver*

$$C:NOAg.$$

In preparing this substance 1 part silver is dissolved in 20 parts nitric acid of sp.gr. 1·36 and 27 parts of 86% spirit of wine added, and the whole gently heated until frothing sets in. The liquid is then removed, and 27 parts or more of spirit added in order to moderate the action. Silver fulminate separates out on cooling (Liebig, *l.c.*; *cf.* Nef, Annalen, 1894, **280**, 308).

Silver fulminate is not formed, as was stated by Liebig (Annalen, 1833, **5**, 287), when nitrogen trioxide is led into an alcoholic solution of silver nitrate (Divers and Kawakita, J.C.S. 1884, **45**, 27), but is only produced by the energetic oxidation of alcohol by nitric acid in presence of silver nitrate. Great caution must be exercised in the preparation of this substance. Capacious vessels should be used, to prevent the liquid boiling over and the formation of a crust of the dry explosive salt on the outside; all flame must be kept at a distance, lest the vapours should take fire; and the mixture should be stirred with wooden rods. The dry salt should be transferred on paper shovels, and kept in paper or cardboard vessels, loosely covered, to prevent explosion from friction.

Silver fulminate crystallises in white opaque glistening needles, scarcely soluble in water, and having a bitter metallic taste.

Silver fulminate is an exceedingly dangerous body, as it explodes much more violently than the mercury salt, by the action of heat, by the electric spark, by friction or percussion, or by contact with sulphuric acid. It even explodes in the moist state, sometimes under water, by friction with a glass rod. It may be rubbed to powder in a mortar with the finger or with a cork. The light accompanying the explosion, which is best seen in the dark, is reddish-white with a tinge of blue (Liebig). When ignited under a pressure of about 2 or 3 mm., it burns slowly with a visible flame. If silver fulminate be thrown into a bottle containing chlorine, it deflagrates before it reaches the bottom, and does not fracture the bottle (E. Davy). Silver fulminate dissolves in hot aqueous ammonia, and the solution, on cooling, deposits crystalline grains of ammonium silver fulminate

$$(C:NO)_2(NH_4)Ag.$$

This salt is sparingly soluble in water, and explodes with much greater violence than the silver salt, even under liquid, when touched with a glass rod (Liebig). Aqueous solutions of the hydroxides of the metals of the alkalis or alkaline earths, or of the sulphides or chlorides of the alkalis, yield similar double salts when boiled with silver fulminate. Copper or mercury can displace silver wholly or in part from silver fulminate. Zinc, even on boiling for several days, displaces only half of the silver, forming silver zinc fulminate. The normal zinc salt is prepared by the action of zinc on mercuric fulminate. By acting on this salt with baryta water, and exactly precipitating the barium from the zinc barium fulminate thus produced with sulphuric acid, zinc hydrogen fulminate is obtained. By saturating this salt with metallic bases, many double salts of zinc fulminate are obtained.

Silver fulminate with triphenylmethyl chloride in benzene gives triphenylacetonitrile oxide, $CPh_3{\cdot}C:N:O$, m.p. 153°, which with HCl gives triphenylacethydroxamyl chloride, $CPh_3{\cdot}CCl:N{\cdot}OH$, m.p. 178–180° (Wieland and Rosenfeld, Annalen, 1930, **484**, 236).

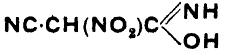
Cadmium fulminate, $Ca(CNO)_2$, is a white powder, stable when dry, but readily decomposed by water, in which it is very soluble. It is one of the most violent explosives, and is nearly as sensitive to shock and heat as mercury fulminate. **Thallous fulminate** becomes yellow on exposure to light, and is the most susceptible of all known fulminates to shock and increased temperature, but the heat of detonation is not high, and its explosion is not violent. **Cuprous fulminate** is insoluble in water, and is almost as violent an explosive as cadmium fulminate, although not so sensitive to shock (L. Wöhler and Martin, Ber. 1917, **50**, 586).

Fulminic acid gives rise to a series of polymerisation products (*v.* FULMINURIC ACIDS).

FULMINURIC ACIDS, $C_3H_3O_3N_3$. *Fulminuric acid.*—This compound was discovered independently by Liebig (Annalen, 1855, **95**, 282) and by Schischkoff (*ibid.* 1856, **97**, 53; 1857, **101**, 213). Its salts are produced by boiling a solution of a metallic chloride or iodide with water and mercuric fulminate:

$$4C\overset{\leftarrow}{:}NOH+H_2O=C_3H_3O_3N_3+CO_2+NH_3,$$

60–75 g. of well-washed mercuric fulminate are boiled with 700–800 c.c. of water, 60 c.c. of saturated ammonium chloride solution are then added, and the mixture is heated to the boiling-point. As soon as a yellow deposit of oxydimercuric ammonium chloride separates, the flame is removed, and ammonia added until all the mercury is precipitated. The solution is filtered, and the filtrate is evaporated, yielding crystalline ammonium fulminurate, which is purified by recrystallisation. This is converted into the basic lead salt by treatment with lead acetate; removal of the lead with H_2S and evaporation yields an indistinctly crystalline mass, which gives colourless prisms of fulminuric acid from alcohol. The silver salt may be decomposed by hydrochloric acid to yield free fulminuric acid. Another method is Ulpiani's (Gazzetta, 1905, **35**, (ii), 357); succinamidedinitrosoperoxide, obtained by the action of fuming HNO_3 upon ethyl acetoacetate, and subsequent treatment with concentrated ammonia, yields an acid proved to be identical with the fulminuric acid of Liebig, together with β-*iso*fulminuramide; the latter yields β-*iso*-fulminuric acid on hydrolysis (*v. infra*). Fulminuric acid decomposes on heating with slight deflagration at 145° (Steiner, Ber. 1872, **5**, 381); heating with dilute acids or alkalis decomposes it into oxalic acid, ammonia and carbon dioxide. Nef (Annalen, 1894, **280**, 329) regards it as nitrocyanoacetamide,



$$NC{\cdot}CH(NO_2)C\begin{matrix}\diagup NH\\ \diagdown OH\end{matrix}$$

Ulpiani (Gazzetta, 1912, **42**, i, 390) represents it as the mono-nitrile of *iso*nitromalonamide, as the ammonium salt yields nitromalonamide when treated with dry HCl in alcoholic solution

$$HO_2N{:}C(CN)CO{\cdot}NH_2 \rightarrow HO_2N{:}C(CO{\cdot}NH_2)_2$$

Ammonium fulminurate forms anhydrous monoclinic crystals, which blacken on heating and give off hydrocyanic acid, ammonia and cyanic acid, the two last uniting to form urea (Liebig).

Potassium fulminurate is prepared by the gradual addition of 2 parts of mercuric fulminate to a saturated solution of 1 part of potassium chloride, followed by gentle boiling until the whole is dissolved. The liquid is filtered hot from a yellowish precipitate, and the compound of mercuric oxide and potassium fulminurate, which separates from the filtrate, is freed from mercury by sulphuretted hydrogen. Recrystallisation from water yields potassium fulminurate in long glistening prisms, which decompose with incandescence when heated to 225° (Schischkoff, *l.c.*).

Sodium fulminurate is converted by a mixture of H_2SO_4 and HNO_3 into trinitroacetonitrile, $C(NO_2)_3CN$.

Silver fulminurate may be obtained by heating ammonium or potassium fulminurate with silver nitrate. It is almost insoluble in cold water, but may be recrystallised from boiling water in long, very thin needles. When heated with concentrated hydrochloric acid in a sealed tube at 110°, traces of oxides of carbon are produced; one-third of the nitrogen is converted into hydroxylamine hydrochloride, while the remainder yields ammonium chloride (Ehrenberg, J. pr. Chem. 1884, [ii], **30**, 55). At 100°, under ordinary pressure, the action is complicated.

The fulminurates of *calcium, strontium, barium, iron* and *lead* may be obtained by double decomposition from the ammonium or potassium salts. On heating an ammoniacal solution of copper sulphate with fulminuric acid, ammonium copper fulminurate,

$$C_3H_2N_3O_3(CuNH_3),$$

is deposited on cooling in characteristic glistening purple prisms.

By passing hydrogen chloride through an alcoholic suspension of potassium fulminurate, Schischkoff (*l.c.*) obtained an oil supposed to be ethyl fulminurate; it is not, however, the ester, but has the composition $C_4H_6EtNO_5$. It readily forms additive compounds with ammonia and the amines (Ehrenberg, *l.c.*). According to Siedel (Ber. 1892, **25**, 2756), fulminuric acid forms two series of esters, the nitrogen-ethyl ester, m.p. 155°, and the oxygen-ethyl ester, m.p. 133°; the latter, $C_3N_3O_2H_2{\cdot}OEt$, is formed by the action of ethyl iodide upon silver fulminurate and when boiled with water is converted into *desoxyfulminuric acid*, cyano-*iso*nitroso-acetamide,

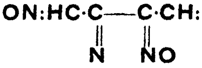
$$C_3H_3N_3O_2=NC{\cdot}C({:}NOH){\cdot}CONH_2,$$

m.p. 184°, a derivative of mesoxalic acid (Nef, Annalen, 1894, **280**, 331).

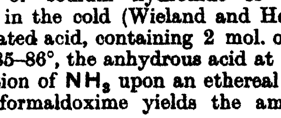
*Metafulminuric acid, iso*cyanuric acid,

$$C_3H_3O_3N_3,$$

is the oxime of *iso*nitroso-*iso*-oxazolone,



(Wieland *et al.*, Ber. 1909, **42**, 1346; Annalen, 1929, **475**, 54; Ulpiani, Gazzetta, 1915, **46**, I, 1). This is obtained by the spontaneous polymerisation of fulminic acid (Scholvien, J. pr. Chem. 1885, [ii], **32**, 461); it is accompanied by small amounts of the tetramer, *iso*cyanilic acid, $C_4H_4O_4N_4$, known to be furoxanedialdoxime,

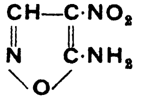


(Wieland, Annalen, 1925, **444**, 7); the latter is characterised by its conversion into a bright red alkali salt with boiling alkali. Metafulminuric acid is best prepared by treating chloroformaldoxime, $CHCl{:}NOH$ with a small quantity of sodium hydroxide or aqueous ammonia in the cold (Wieland and Hess, *l.c.*). The hydrated acid, containing 2 mol. of water, melts at 85–86°, the anhydrous acid at 102°.

The action of NH_3 upon an ethereal solution of chloroformaldoxime yields the ammonium salt of *cyanoisonitroso-acethydroxamic acid*, or *oximino-cyanoacethydroxamic acid*,

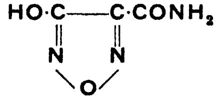
$$C_3H_3O_3N_3 = HON{:}C(CN)C(OH){:}NOH;$$

the ammonium salt is decomposed by hydrochloric acid, yielding the acid, which crystallises from ether in colourless cubes, m.p. 117–118° (Nef, Annalen, 1894, **280**, 321). Wieland and Hess (*l.c.*) found that 1 equivalent of alkali converts metafulminuric acid quantitatively into the above, which is isolated by the addition of acid (it is not reconverted to metafulminuric acid). This reaction goes spontaneously in the absence of alkali (Ulpiani, Gazzetta, 1915, **46**, i, 1), but is accelerated by heat or alkali. Cyano*iso*nitrosoacethydroxamic acid can undergo further changes in three directions. In aqueous solution or in organic solvents it is converted into an impure form of the syrupy fulminuric acid of Ehrenberg (*see below*). The anhydrous form is converted at 70° into *a-amino-β-nitro*-iso-*oxazole*,

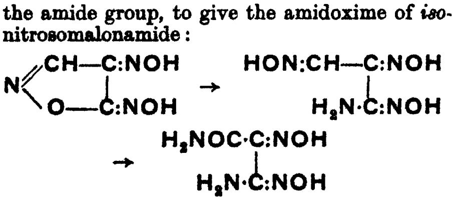


When allowed to stand in glass vessels in the hydrated or anhydrous form, it changes to *iso*fulminuric acid.

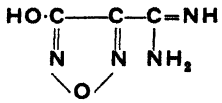
Iso*fulminuric acid*, $C_3H_3O_3N_3$, is 3-hydroxyfurazan-4-carboxylamide,



It is best prepared from the mixture of solids obtained by the interaction of ammonia and chloroformaldoxime; it can also be obtained directly from metafulminuric acid and ammonia, or Na_2CO_3 (1 mol.), by heating for a few minutes on the water-bath; and by the decomposition of metafulminuric acid in a sealed tube. It has m.p. 202° (decomp.). It is soluble in alcohol, acetone and ether. On hydrolysis with boiling baryta water it yields 3-hydroxyfurazan-4-carboxylic acid, m.p. 174° decomp. (Wieland and Baumann, Annalen, 1912, **392**, 196). These authors have shown that *iso*fulminuric acid is not the direct product of the action of NH_3 upon chloroformaldoxime, or upon the cyano*iso*nitroso-acethydroxamic acid (*see above*) of Nef. With bases, chloroformaldoxime loses HCl to form fulminic acid, which polymerises to metafulminuric acid; this can react further with ammonia, with ring-fission and simultaneous conversion of the aldoxime to the amide group, to give the amidoxime of *iso*nitrosomalonamide:

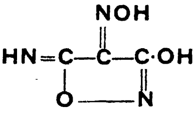


This is converted by alkali into the above acid of Nef, and also into the compound $C_3H_4O_2N_4$ of Ehrenberg (*l.c.*), by dehydration between two =NOH groups and addition of NH_3 to the —CN group: the compound being 3-hydroxyfurazan-4-carbonamidine,

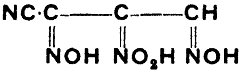


Both of these substances are formed by the action of NH_3 upon chloroformaldoxime, *i.e.* upon metafulminuric acid. They are the precursors of *iso*fulminuric acid, and are converted into this acid by warm ammonia.

In the preparation of *iso*fulminuric acid from metafulminuric acid by the action of sodium carbonate, small quantities of another isomer, m.p. 143° (decomp.), are also obtained. This is 3-hydroxy-4-*iso*nitroso-*iso*-oxazolonimide



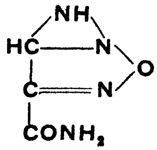
*Iso*fulminuric acid is also obtained by loss of CO_2 from a tetramer of fulminic acid, *pericyanilic* acid:



$$\begin{array}{ccc} NC\cdot C & —\,C\,— & CH \\ \| & \| & \| \\ NOH & NO_2H & NOH \end{array}$$

(Wieland and Kitasato, *ibid.* 1929, **475**, 54).

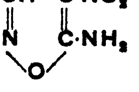
By boiling furoxandicarboxylamide with water, Ulpiani (Gazzetta, 1912, **42**, I, 375) obtained fulminuric acid and two new isomers, β- and γ-fulminuric acids. The β-acid is present as the amide, m.p. 175°,



which is very stable to acids, and can be recrystallised from boiling conc. hydrochloric acid. Thus *β-fulminuric acid* is seen to be *imidofurazan-carboxylic acid.* It has m.p. 196° and is soluble in organic solvents and boiling water. It gives no colour with ferric chloride; silver and mercuric nitrates give insoluble precipitates. Copper acetate slowly precipitates large transparent green crystals, insoluble in cold water. The acid gives an ester by the action of alcoholic HCl. It also gives a nitroso-derivative, $C_3H_2N_3O_3\cdot NO,H_2O$, which explodes at 133°; the mother-liquors from this preparation give the ammonium salt of *iso*nitroso-cyanacetic acid, m.p. 103°:

$$CN\cdot C({:}NOH)\cdot COOH.$$

The *γ-fulminuric acid* is 5-amino-4-nitro-*iso*-oxazole, m.p. 247°,



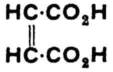
An aqueous solution is not precipitated by copper acetate, nor coloured by ferric chloride, it gives a precipitate with mercuric nitrate but not with the chloride. It is a very weak acid; it does not give an ammonium salt, nor is it esterified by alcohol and HCl; it gives no nitroso-derivative. When boiled with baryta, it eliminates NH_3 to give 5-hydroxy-4-nitro-*iso*-oxazole, $C_3H_2O_4N_2,H_2O$.

The *fulminuric acid*, $C_3H_3N_3O_3$, of Ehrenberg is obtained by treating cyano*iso*nitrosoacethydroxamic acid with NH_3; it is a powder, which chars without melting when heated (Nef, *l.c.*; Ehrenberg, J. pr. Chem. ,1884, [ii], **30**, 55).

FULVENES (*v.* Vol. III, 534*b*, *c*).

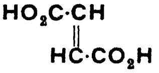
FULVIC ACID (this Vol., p. 53*d*).

FUMARIC ACID and MALEIC ACID. These two ethylene-*αβ*-dicarboxylic acids form the classical example of geometrical (*cis-trans*) isomerism. Maleic acid readily forms an anhydride, whereas fumaric acid does not; on the basis of this and other evidence maleic acid is assigned the *cis-* and fumaric acid the *trans-*configuration.



$$\begin{matrix}HC\cdot CO_2H\\ \|\\ HC\cdot CO_2H\end{matrix}$$

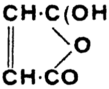
cis-



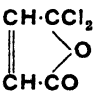
$$\begin{matrix}HO_2C\cdot CH\\ \|\\ HC\cdot CO_2H\end{matrix}$$

trans-

The oxidation of benzoquinone to maleic acid with nascent silver peroxide (Kempff, Ber. 1906, **39**, 3715) is in agreement with this view as is, indeed, the vapour-phase oxidation of benzene itself (*v. infra*). On the basis of chemical evidence, Anschütz (Annalen, 1887, **239**, 164; 1928, **461**, 155) assigned to maleic acid the hydroxy-lactone structure



Physical evidence for this cyclic structure has been put forward by Wassermann and Smakula (Z. physikal. Chem. 1931, **155**, 366) and by Dadieu, Pongratz and Kohlrausch (Sitzungsber. Akad. Wiss. Wien, Math. Naturw. Kl. Abt. II, 3, 1931, **140**, 353). The analogous structure,



has been assigned to maleyl chloride in view of its abnormal reactivity (Ott, Annalen, 1912, **392**, 245).

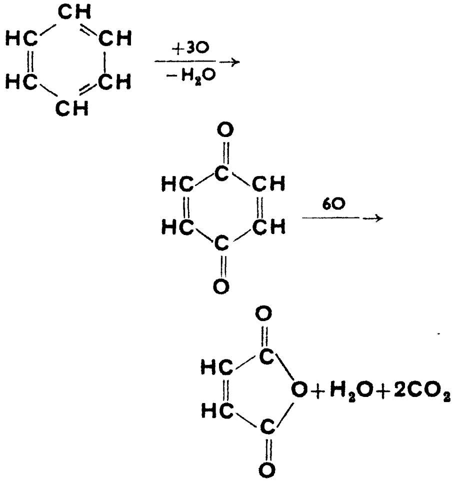
Fumaric acid occurs widely distributed in the plant kingdom (*e.g.* in Iceland moss and the common fumitory); in the animal world it plays a vital part in respiratory processes (*cf.* Szent-Györgyi, Z. physiol. Chem. 1935, **236**, 1). Maleic acid does not appear to occur in nature.

Fumaric acid is produced, together with maleic anhydride, when malic acid is heated to 150° (Wislicenus, Annalen, 1888, **246**, 91; Michael, J. pr. Chem. 1892, [ii], **46**, 231) or boiled with sodium hydroxide solution (Fichter and Dreyfus, Ber. 1900, **33**, 1453), by heating halogenated succinic acids (Brunner and Chuard, *ibid.* 1897, **30**, 201) and, synthetically, by condensation of glyoxylic and malonic acids under the influence of pyridine:

$$CO_2H\cdot CHO+CH_2(CO_2H)_2 \xrightarrow[-CO_2]{-H_2O} CO_2H\cdot CH{:}CH\cdot CO_2H$$

(Doebner, *ibid.* 1901, **34**, 53). Technically, fumaric acid may be prepared by the *Aspergillus fumaricus* fermentation of certain carbohydrates (B.P. 146411; Walker, J.S.C.I. 1930, **49**, 946; *v.* this Vol. 50*c*), while the most convenient method for its laboratory preparation is the oxidation of furfural with sodium chlorate in the presence of a small amount of vanadium pentoxide (Milas, Organic Syntheses, 1931, **11**, 46).

Maleic acid was formerly best obtained by the slow distillation of acetylmalic anhydride (Anschütz, Ber. 1881, **14**, 2791) or by heating malic acid with phosphorus pentachloride to 200–220° (van der Riet, Annalen, 1894, **280**, 216). At the present time, however, maleic acid and its anhydride are prepared on the large scale by the vapour-phase oxidation of benzene using a vanadium pentoxide catalyst:



a process which was first worked out in 1916 by Weiss and Downs (U.S.P. 1318631, 1318632); a large number of patents describing improvements in this process have appeared and the reader is referred for further information to summaries by Weiss and Downs (Ind. Eng. Chem. 1920, **12**, 228; J.S.C.I. 1926, **45**, 188T) and to Hilditch, "Catalytic Processes in Applied Chemistry," 1929, pp. 199–205.

Fumaric acid may be converted into maleic anhydride by heating or by treatment with phosphorus pentachloride, phosphorus oxychloride or phosphorus pentoxide (Volhard, Annalen, 1892, **268**, 255; Tanatar, *ibid.* 1893, **273**, 31). Maleic acid is converted into fumaric acid by heating in a sealed tube at 200° (Tanatar, *l.c.*) or even by long standing in the dark in aqueous solution (Kailan, Z. physikal. Chem. 1919, **93**, 613). This change is also brought about by sunlight or ultra-violet light, especially in the presence of a trace of bromine (Ciamician and Silber, Ber. 1903, **36**, 4267; Wislicenus, Ber. Sächs. Akad. Wiss. 1895, 489; Kailan, Z. physikal. Chem. 1914, **87**, 333; Warburg, Sitzungsber. Preuss. Akad. Wiss. Berlin, 1918, 1228).

Fumaric acid is difficultly soluble in cold water and crystallises from hot water in small, colourless needles which sublime without melting in an open tube at 200°, but which melt in a sealed tube at 284°. Maleic acid forms monoclinic prisms, m.p. 135°, which boil at 160° with anhydride formation.

Fumaric and maleic acids may be distinguished by the crystalline form of certain salts (especially the silver, copper, lead and mercury salts) (van Itallie, Pharm. Weekblad. 1922, **58**, 1312; Wagenaar, *ibid.* 1927, **64**, 6); fumaric acid is also distinguished by the fact that its mercury salt is quantitatively precipitated in the presence of dilute nitric acid (Ölander, Z. physikal. Chem. 1929, **144**, (A), 49). The following esters may be recommended for purposes of identification: p-*nitrobenzyl fumarate*, m.p. 150·8°, *maleate*, m.p. 89·3°; *phenacyl fumarate*, m.p. 197·5°, *maleate*, m.p. 119°; p-*phenylphenacyl maleate*, m.p. 168°.

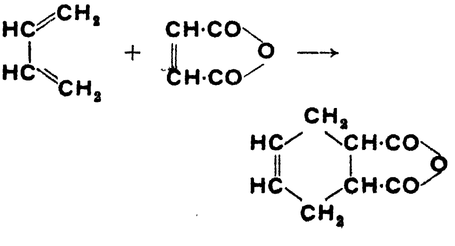
Both fumaric and maleic acids yield acetylene on electrolysis of their alkali salts and both may be reduced to succinic acid. With bromine fumaric acid yields *meso*-dibromosuccinic acid and maleic acid, *rac*-dibromosuccinic acid; these reactions are examples of *trans*-addition (McKenzie, J.C.S. 1912, **101**, 1196). With potassium permanganate, however, *cis*-addition takes place with the formation of racemic acid from fumaric acid and of *meso*tartaric acid from maleic acid (Kekulé and Anschütz, Ber. 1880, **13**, 2510; 1881, **14**, 713).

DERIVATIVES.

Esters. *Diethyl fumarate* is best obtained by esterification of the acid with alcohol vapour in a special apparatus (Corson, Adams and Scott, Organic Syntheses, 1930, **10**, 48). *Dimethyl maleate* is conveniently prepared from the anhydride (Clemo and Graham, J.C.S. 1930, 213). Alkylene oxides have also been recommended for esterifying maleic acid (G.P. 544288).

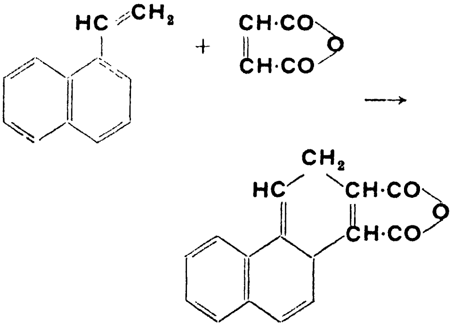
Maleic anhydride is usually obtained directly in the vapour-phase oxidation of benzene but may be prepared by distillation of the acid with a neutral solvent such as xylene (Mason, J.C.S. 1930, 700) or *in vacuo* with phosphorus pentoxide (Terry, J. Amer. Chem. Soc. 1925, **47**, 1067); on the large scale the anhydride may be produced by vacuum distillation of the acid without added reagent (U.S.P. 1901914, 1966853).

Maleic anhydride forms needles or prisms, m.p. 53°, b.p. 202°, having a faint unpleasant odour. It is principally remarkable for the ease with which it combines with compounds containing conjugated double bonds to form cyclic products, *e.g.*



(Diels and Alder, Ber. 1929, **62**, 2081, 2087; 1930, **63**, 2662; Annalen, 1931, **490**, 243; Alder and Stein, *ibid.* 1934, **514**, 1). This reaction usually takes place readily in benzene solution, sometimes being brought to completion at room temperature; it has found wide application, not only in synthetic work but also in the detection of conjugation in natural products. Maleic anhydride is now, in fact, one of the most valuable reagents in both synthetic and analytic organic chemistry.

Maleic anhydride also forms co-polymers with ethylenic compounds, *e.g.* stilbene (Wagner-Jauregg, Ber. 1930, **63** [B], 3213; Annalen, 1931, **491**, 1) while, more recently, it has been found that some compounds of the styrene type yield maleic anhydride adducts as do ordinary conjugated compounds, *e.g.* vinylnaphthalene:



(Cohen and Warren, J.C.S. 1937, 1315).

APPLICATIONS.

The development of the vapour-phase oxidation process has made maleic acid and anhydride, formerly chemical rarities, into relatively cheap materials and many uses for them have been proposed. Downs (Ind. Eng. Chem. 1934, **26**, 17) gives a review of possible technical applications. Some of these depend on the reaction of maleic anhydride with dienes; thus, Martin, Griese and Lowy (*ibid.* 1933, **25**, 381) suggest the use of maleic anhydride for the removal of readily oxidised dienes from petroleum; similarly U.S.P. 1898363 advocates the use of maleic anhydride as a stabiliser for unsaturated oils. Adducts from maleic anhydride and various terpenes form the basis of synthetic resins described in U.S.P. 1993025–1993037. Maleic and fumaric esters, their polymers and copolymers with other substances have been proposed for use as plasticisers, resins, etc. (G.P. 512321, 553174; U.S.P. 1945307, 1969482).

H. N. R.

FUMARINE syn. **PROTOPINE**,

$C_{20}H_{19}O_5N$,

an opium alkaloid.

FUMIGATIN (this Vol., p. 54*a*).

FUMIGATION OF WAREHOUSES AND SHIPS AGAINST VERMIN AND PESTS OF STORED PRODUCTS.—Vermin and human parasites are a menace to health. They are worse in hot countries than in temperate, though even in these, wherever conditions are insanitary, they are dangerous.

The amount of illness caused by vermin and human parasites is great though difficult to estimate. The increase of world transport and of bulk storage has greatly accentuated the ravages of vermin and insects. Whilst quarantine arrangements have had some success, in localising particular pests of growing plants, there has been less effort and less success with the pests of stored goods. Many of the important pests are now cosmopolitan, even those native to hot countries managing for the most part to over-winter in a resting stage in temperate climates. The direct loss to industry by pests in the U.S.A. and in Germany together has been estimated at eighty million pounds sterling annually. Whilst improvement of conditions of transport and storage, if based on ecology, will do much to decrease these losses they can be greatly reduced at once by proper control measures of which fumigation is one of the most important, others being spraying of contact insecticides and dusting with inert dusts.

Adequate control of pests of stored products generally involves the use of two or more measures in combination, *e.g.* spraying premises and dusting goods or spraying premises and fumigating goods. To be really effective, however, all such systems of control must be accompanied by constant inspection of stock and premises and continual cleaning of premises, segregation of goods, etc. The general improvement in hygiene which is brought about is one of the strongest arguments in favour of fumigation, spraying and similar methods of control.

The object of fumigation is the exposure of pests to a gas poisonous to them at a sufficient concentration for a sufficient time to kill them without injuring the products on which they are feeding or the materials of the ship or warehouse in which the products are lying. The choice of a fumigant depends mainly on the relative importance of the following factors: Toxicity; molecular weight; vapour pressure, if boiling above room temperature; chemical activity, notably action on water, fats, sugars and enzymes found in stored seeds, roots, etc.; liability to taint goods; cost; toxicity to man; ease of transport and of application; inflammability. There are comparatively few compounds with sufficient toxicity and volatility and sufficiently cheap and harmless to man. Of these some are ruled out by reason of price while of the remainder many are dangerously inflammable.

Determination of Toxicity.—This may be made under controlled conditions in the laboratory or under normal conditions in buildings or ships. The insects must be identified precisely since their resistance varies with the species and strain, the age and stage of development and with the cultural conditions. These conditions include food, temperature, humidity, amount of space per insect, age of culture and freedom from parasites and pathogenic bacteria. Response to a change in conditions is seldom rapid so that it is advisable to breed insects under the same conditions as those under which they are to be fumigated (Cotton, J. Econ. Entomol. 1932, **25**, 1088). In a determination, the insects must be exposed, under suitable conditions, to a known concentration of fumigant for a given time. If the insects are to be tested in the warehouse, the concentration actually attained, at various times during the fumigation, must be measured. This is also desirable in laboratory experiments, except in preliminary or in comparative experiments, in which the concentration may be assumed to remain at the calculated value throughout.

In all improved forms of apparatus a mixture of air and fumigant is passed through a chamber containing the insects. It may then be allowed to escape as in the continuous flow methods (Niefert and Garrison, U.S. Dept. Agric. Bull., No. 893, 1920; Cupples, Ind. Eng. Chem. [Anal.], 1933, **5**, 36), or it may be passed back again, or alternatively it may be circulated. In continuous-flow methods two streams of air, one of which is saturated with fumigant at a given temperature, are mixed in the required proportions by regulating the rate of flow of each, as indicated by flow-meters. The air may be conditioned to a definite temperature and humidity. Samples may be taken for analysis. The method is probably best suited to the less volatile fumigants. In " oscillation " or " circulation " methods (Bovingdon, Ann. Appl. Biol. 1934, **21**, 704), one or more large non-absorptive reservoirs are dosed with sufficient fumigant to give the required concentration, which is checked at different times by an analysis of small samples. The whole system can be made vacuum-tight and, by preliminary evacuation, the requisite amounts of water vapour, dry air and the separate components of the fumigant can be introduced. This may be done without affecting the insects. Alternatively the apparatus allows of fumigation under reduced pressure. The circulating gas may be divided into two streams one of which serves to keep the mixture uniform, since some change of composition by absorption is unavoidable, and the other passes through the insect chamber. By making this a bye-pass circuit and inserting a simple valve, the rate of passage through the insect chamber may be regulated.

The percentage kills actually obtained in an experiment are replaced by dosages inferred on the assumption that there is a normal distribution of susceptibility. These inferred dosages are expressed in suitable units and are then plotted against the logarithms of the corresponding observed dosages and are generally found to give a fairly straight line, which may be arrived at by calculation or by inspection. Weighting coefficients, for each observation, can be determined from this line and a more accurate line derived. It is also possible to determine whether the observations depart further from the line than would be expected by chance, in which case there is either a real departure from the simple proportionality or uncontrolled experimental conditions are causing undue fluctuations (Bliss, Ann. Appl. Biol. 1935, **22**, 134). One great advantage of this method of expressing results is the great increase in accuracy it affords in arriving at the dosage required, with any given number of insects, which may be expected to give 100% mortality. The straight line, above described, can be readily extrapolated, and the logarithm of the dose corresponding to a percentage mortality as near as is required to 100% can be read off. The accuracy of this value will vary with the departure of the observations from the line. The term dosage refers to a combined concentration–time quantity. From the results of a large number of experiments Peters (Sammlung chemischer Vorträge, No. 31, 1936, Chemie und Toxikologie der Schädlingsbekämpfung) considers it to be represented by the product of concentration of the fumigant multiplied by the time of exposure and that the toxic effect is proportional to this product. This relation is the same as that obtaining in the action of poisons on mammals and is known commonly as Haber's rule.

It seems that this is approximately true within limits for the separate quantities. In a practical fumigation the concentration is continually varying and the toxic effect may therefore be expected to be proportional, within the same limits, to the value of the concentration–time integral or the area under the time–concentration curve.

The lowest satisfactory number of test insects is about thirty. The greater the number, the greater the accuracy with which the dose likely to give a desired percentage kill can be determined. In the control of a heavy infestation, the percentage kill required may lie very close to one hundred and its determination will require a large number of test insects. By using large numbers of insects Pratt, Swain and Eldred (J. Econ. Entomol. 1931, **24**, No. 5, 1041) succeeded in showing an effect of protective stupefaction on preliminary exposure to sublethal doses of hydrogen cyanide which is of great importance in the fumigation of citrus trees. Gough (Ann. Appl. Biol. 1939, **26**, 353) found that the offspring of resistant individuals of *Tribolium confusum* were more resistant to hydrogen cyanide than the offspring of susceptible individuals. The selection of a resistant strain, by partially effective fumigation, was suggested by Boyce (J. Econ. Entomol. 1928, **21**, 715).

Attempts to determine penetration of a fumigant into goods by observing the toxic effect on test insects in small containers buried in the goods are often unsatisfactory owing to local disturbance of the texture of the material of the goods and to alteration of the susceptibility of the insects. It is generally better to determine the concentration at various points within the material by sampling and analysing the atmosphere at these points.

Vaporisation of Fumigants.—Most fumigants are supplied in the liquid form. The method of vaporising them varies with the volatility of the liquid, the prevailing temperature and with the type and size of building fumigated. Moderately volatile liquids, such as hydrogen cyanide, carbon disulphide and methyl bromide are still, sometimes, applied by being poured into shallow pans and allowed to evaporate. Frequently volatilisation is assisted by immersing a heated coil in the liquid or by passing the liquid through a heated coil (Osburn, New Jersey Dept. Agric., Circular 188, 1930; Page and Lubatti, J.S.C.I. 1933, **52**, 316T). Application of heat is particularly desirable with a substance such as hydrogen cyanide which has a large latent heat of vaporisation.

Another method of application consists in spraying, under pressure, through fine nozzles. Ethylene oxide mixed with carbon dioxide, hydrogen cyanide and chloropicrin are often applied in this way. One objection is the danger of soaking certain porous goods or fabrics and hence of objectionable residues or of delayed vaporisation (Page and Lubatti, J.S.C.I. 1933, **52**, 323T). Screens of suitable fabric have been used to provide a large evaporating surface for the relatively non-volatile fumigant heavy naphtha (Ashmore and McK. Hughes, Brit. Med. J. 1937, i, 459).

A more generally satisfactory method of application is that of heating the liquid in an apparatus called a vaporiser. Different types are described in the sections dealing with the common fumigants.

Methods of Determination.—The concentration of fumigant in the air can be determined by the following methods:

1. Aspirating a known volume of air and fumigant through bubblers containing absorbing solutions, in which the fumigant is subsequently determined (Eddy and Geddings, J. Econ. Entomol. 1929, **22**, 366).
2. Collecting a known volume in an evacuated vessel which either contains the absorbent solution or is provided with means for adding it later.
3. Physical or physico-chemical methods in which a change of concentration is shown by the change of the electrical resistance of a hot wire, following a variation in its temperature. This may depend only on the thermal conductivity of the gas, as in the *Catharometer* (Daynes and Shakespear, Proc. Roy. Soc. 1920A, **97**, 273), or on the change in the rate of catalytic combustion of the inflammable fumigant around the hot wire, which is itself the catalyst.
4. Comparison of the refractive index of the air–fumigant mixture with that of a standard gas, by means of a differential refractometer (Taylor, Chem. and Ind., 1939, **58**, 1078).

The catharometer is not of general applicability since it is unduly sensitive to small changes of concentration of carbon dioxide and water vapour which occur in goods.

Apparatus depending on catalytic combustion is especially suited to routine determination of concentration in the main space of a fixed chamber. The differential refractometer method is cumbersome and needs a costly apparatus and a large sample of gas. The aspiration method has the following disadvantages:

(*a*) Dead space in connecting tubes, etc., makes it impossible to take a very small sample.

(*b*) Inconvenience of using an aspirator or pump, except at a fixed chamber.

(*c*) Inapplicability to sampling from chambers under reduced pressures.

(*d*) Difficulty of collecting a large number of samples within a very short period.

(*e*) Difficulty of sampling from a large number of points owing to the amount of flexible tubing required.

The method of collecting the gas sample in an evacuated vessel is of wider application than the others and has been considerably developed.

In a recent form the evacuated vessel is opened electrically from outside the space being fumigated. Samples from hidden spaces, such as the interior of packed goods or the spaces in hollow walls, are obtained by attaching to the vessel a capillary tube which is inserted into the space (Page, J.S.C.I. 1935, **54**, 421T; Lubatti, J.S.C.I. 1935, **54**, 424T).

The error in sampling from hidden spaces produced by adulteration of the sample by gas drawn in from the main space can be obtained from the formula, $x=[a+b(m-1)-(a-b)e^{-m}]/mV$ where V=volume of intergranular space, mV=volume of sample, a/V=initial concentration of fumigant in intergranular space, b/V= concentration of fumigant in surrounding space and x=concentration of fumigant in sample.

Since the intergranular spaces of goods vary greatly with their nature and method of packing, the calculation of this error is of some importance. In general the percentage intergranular space is surprisingly large. Some representative values are: tobacco in cask, 60; flour, 49; grain, 45; currants and raisins (in 56-lb. boxes), respectively 33 and 26; dates (in block), 2 (Page and Lubatti, J.S.C.I. 1937, **56**, 54T).

Residual fumigant in goods or building materials after fumigation and airing is usually recovered either by distillation or by dry aeration or by aeration of a suspension in a suitable liquid which is generally heated. The fumigant in the air stream is absorbed in a reagent and determined.

Time–Concentration Curves.—Since the toxic effect of a fumigant is proportional, within limits, to the product of the concentration and the duration of exposure, a series of curves, for representative positions, gives a fair idea of the efficacy of a fumigation. Curves have been found generally to conform to one of four types (Page, Lubatti and Gloyns, J. Hygiene, 1939, **39**, 12), Fig. 1.

Type I curves represent the change of concentration in the main space being fumigated; a maximum is reached soon after the end of vaporisation and thereafter the concentration falls, more or less rapidly, according to the leakiness of the building and the absorptive nature of its fabric and contents. When airing begins, as indicated by the dotted line, there is a rapid and continuous fall in concentration. The value of the maximum is usually about ½ to ⅔ the calculated concentration. Type II curves represent the change of concentration in spaces such as cupboards to which the fumigant is conveyed by diffusion and convection from the main space, there being no direct application of fumigant. The curves are similar to those obtained for the main spaces except that the maximum concentration attained is lower and is reached later.

A curve of type III is frequently obtained by sampling from lath and plaster partitions. A curve of type IV is characteristic of the change of concentration inside piles of absorbent material such as heaps of clothes. It will be seen that airing in types III and IV is very slow. In the fumigation of ships similar spaces are met with and similar curves are found (Stock, Monier-Williams, Page, Lubatti and White, Bull. Off. internat. Hyg. Publ. 1933, **25**, 293).

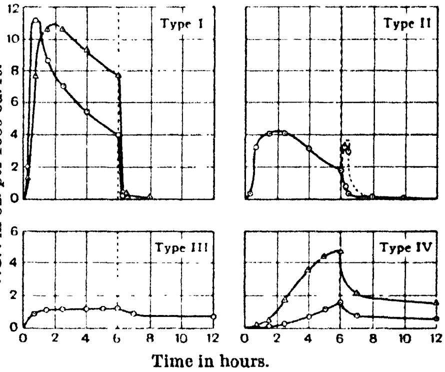


Fig. 1.

In the fumigation of empty warehouses for disinfestation of the fabric the curves obtained are of type I, but big differences are found depending on the ratio of the volume of the building to the surface area, on the absorptive nature of the fabric and on the air-tightness.

Most unpainted building materials are absorptive. This absorption is very greatly reduced by two or three coats of oil paint. The most leaky part of a building is usually the roof, but a boarded and felted roof is relatively air tight (Page and Lubatti, J.S.C.I. 1933, **52**, 309T).

The construction of buildings and the materials of construction influence penetration into cracks and hidden spaces. Materials vary greatly in their transmissive properties. In tall, single storey warehouses the concentration is frequently too low near the ridges of the roof and can best be raised by stirring the whole of the air in the warehouse.

Curves obtained when sampling from inside packages of goods approximate to type III, if the difficulty in penetrating the package is due chiefly to the packing material, and show more resemblance to type I or II, if most of the loss of fumigant is due to absorption in the goods. For example, the concentration inside a 56-lb. block of dried fruit follows the concentration in the main space, type I curve, if there is no packing material, but, as the block is enclosed first in parchmentised paper and then also in a wooden box the curves obtained approximate more to types II and III. Unless the fruit is extremely moist, there is practically no gradient of concentration within the box. With other substances such as flour in sacks and tobacco in casks or bales there is a very steep gradient. The construction of cases as well as the material used for them influences penetration.

With curves of type III airing is slow and after the end of the fumigation a useful concentration of fumigant remains for a considerable period, during which fumigation continues.

It appears that the main source of loss of most fumigants is absorption in goods or porous materials, although there are few published data.

For a particular product the most important variables are: concentration of fumigant, temperature, humidity and water content of the product. The rate of absorption is important as well as the total amount of fumigant absorbed at equilibrium.

Greatly improved distribution and penetration are secured if goods are stacked in narrow piles with narrow alley-ways between. Boxed goods lend themselves to such systems of stacking. Dried fruit, for example, is stacked for fumigation, in tiers one box wide, with spaces of about 2 in. between the tiers, the two ends of each box being exposed to an alley-way. Cacao in bags cannot be stacked in piles narrower than two bags wide. In this way one end of every bag is exposed to an alley-way and the penetration is considerably better than when the piles are three or more bags wide (Page and Lubatti, J.S.C.I. 1933, **52**, 323T; Burns Brown, *ibid.* 1937, **56**, 116T).

It has been found best to fumigate goods in specially constructed chambers rather than in ordinary warehouses. These chambers have fixed characteristics so that the behaviour of fumigant in them can be foretold and conditions repeated and goods can be stacked in them in a standard way, an even distribution is thus assured and the concentration checked. The chambers can be of such a size as to allow of a repeat fumigation, if necessary, without undue expense, and they can be fitted with heating, vaporising, circulating and airing devices which make for economy and safety. Chambers designed to operate at atmospheric pressure are made of iron, bituminous felt or brick, well plastered and painted. If intended for fumigants, without appreciable fire-hazard they may be heated by internal sealed, electric tubular heaters. For other fumigants, heaters must be external or must consist of steam or water pipes. Any form of heating except hot water is dangerous for use with carbon disulphide. Steel barges are used successfully as fumigation chambers. Oil-dressed tarpaulins used to cover the hatches are very nearly gas-proof. Care must be exercised in sheeting down and the barges must be regularly overhauled.

Chambers working under reduced or under slightly reduced pressure must be made of mild steel. They are now provided with circulating apparatus as well as with vacuum pumps. Some have interlocked doors, valves, etc., to ensure that no possible leakage can occur, and are now used where it is essential that no trace of fumigant should escape into the building in which they are housed. In multiple plant a certain amount of fumigant may be saved after the fumigation and passed to a second unit. The cycle of operation in chambers working at reduced pressure varies considerably from one company's recommendations to another. In general, unless the goods to be treated are not very absorptive, only slight improvement in penetration is brought about by the use of highly reduced pressures. Claims have, however, been made for an increase of toxicity and decrease of absorption by pre-fumigations with carbon dioxide carried out in chambers working at reduced pressures (Young, Wagner and Cotton, J. Econ. Entomol, 1937, **30**, No. 3, 560; Peters, Anz. Schädlingskunde, 1936, **12**, No. 7, 82; Lindgren, J. Econ. Entomol. 1936, **29**, 1132; Lepigre, Chim. et Ind. 1934, **32**, 1263; Page and Lubatti, Nature, 1937, **139**, 553).

The advantage of the circulation of the fumigant, which is obtained in chambers, can also be obtained in storage silos by fitting them with special fans and piping. The alternative way of dealing with large bulks of grain, etc., is to mix with it, during loading, a material which will slowly give off a fumigant. Such a material is calcium cyanide, which reacts with water vapour, and with carbon dioxide to liberate hydrogen cyanide; another is ethylene oxide, cooled by mixing with solid carbon dioxide; whilst a third, which is used in Germany, is aluminium phosphide which generates phosphine by reaction with water vapour.

The most important fumigants will now be considered in detail; the general chemistry of the gases employed will be found in other articles of this Dictionary.

Hydrogen Cyanide.—This is one of the oldest fumigants and one of the commonest at the present day. It has a high toxicity to rats and to most insects. Certain beetles such as *Calandra granaria* and *Trogoderma kharpa* are very resistant. It is inflammable but not dangerously so, and considering its efficiency it is not unduly costly.

Methods of Application.—In the original method it was generated in the space to be fumigated by the interaction of sulphuric acid diluted 1:2 by volume and sodium cyanide, the interaction of a solution of the cyanide and chlorate of sodium with concentrated hydrochloric acid was also used, 2 g. of cyanide and 1 g. of chlorate were dissolved separately and the solutions mixed. To this was added 10 c.c. of acid. A mixture of hydrogen cyanide and cyanogen chloride was evolved. In using the sulphuric acid method it is essential that the acid be freshly diluted so as to be hot when the cyanide is introduced. In practice vats or tubs were generally used and the cyanide tipped in from swivel boxes by means of a cord. It has been considered safer to pour a solution of cyanide into more concentrated acid through tubing (Stock and Monier-Williams, Min. Health Rep. on Health and Med. Sub. No. 19). A booklet by the Roessler and Hasslacher Chemical

Co. (N.Y. 1932) gives the latest development of this so-called " dumping " or " pot " method.

The gas may be introduced by vaporisation of liquid hydrogen cyanide, b.p. 26·5°. The liquid, stabilised by small amounts of acid, commonly oxalic acid, is generally stored in steel cylinders, but sometimes in small iron drums with double screw caps or in stout glass bottles with crown cork stoppers.

It is applied in three ways: (1) By pouring it into shallow pans on the floor or on to the floor itself by operators wearing gas masks. (2) By forcing it, by means of air-pressure, through screwed iron tubing, terminating in spray nozzles, dosage being controlled by weighing. The tubing may be installed temporarily, or permanently when the nozzles may be fixed inside the machinery of mills, etc. (Wagner, Cotton and Young, U.S. Dept. Agric. 1936, " The Machinery Piping System of Flour Mill Fumigation "). (3) By evaporating it in vaporisers. A small vaporiser for hydrogen cyanide consists of an open conical vessel with a removable lid; the hydrogen cyanide, which has been poured in, is boiled off by means of electrical heaters in good thermal contact with the bottom of the vessel. The vaporiser is placed inside the space to be fumigated and the heaters connected to a source of supply outside. When all the liquid has evaporated, the temperature of a fusible link rises until it melts and breaks the circuit by actuating a mercury switch. This apparatus is not suitable for the fumigation of large buildings owing to the high electric loading required. Vaporisers with a large reserve of heat may be used, together with some method of transferring the liquid hydrogen cyanide to them after the sealing of the building for fumigation (Page and Lubatti, J.S.C.I. 1933, **52**, 316T; Akin and Sherrard, U.S.P.H. Repts. 1928, **43**, No. 41, 2647; Walker and Eldred, Ind. Eng. Chem. 1925, **17**, 1074). Liquid hydrogen cyanide may also be absorbed in granular material, *e.g.* kieselguhr. The proprietary product, " *Zyklon B* " contains also a stabiliser and lachrymator, generally a mixture of a simple chloro-ester and bromo-ester. It is sealed in cans which are opened with a special tool, covered with a rubber cap and placed in position. Operators, wearing gas masks, remove the caps and distribute the granules on the floor or on pieces of sacking, etc. The evolution of cyanide is often complete within about fifteen minutes. After aeration the residue is disposed of safely. If the material is used in conjunction with chambers a special vaporiser is sometimes installed. This is placed in a gas-circulating circuit and may function either by passing hot air through the material after perforation of the ends of the container or by spreading the material over a water-jacketed surface after cutting out the lid and inverting the container (Heerdt, Vehr. deutsch. Ges angew. Entomol. 1924, July; Buttenburg and Deckert, Z. ges, Kälte-Ind. 1925, **32**, 17; Beatty, J.R.A.M.C. 1926, **47**, 59; Jäckel, Prakt. Desinfekt. 1927, **19**, 35; Böttcher, Desinfekt. u. Gesundheitsw. 1927, **19**, 143; Akin and Sherrard (*l.c.*); Gassner, Z. hyg. Zool. Schädlingsbekämpf. 1937, **29**, No. 6, 176). Liquid hydrogen cyanide is also available absorbed in discs of wood pulp and stabilised, generally with acetic or sulphuric acid. These discs are very convenient for the fumigation of small spaces (Williams, U.S. Publ. Health Rep. 1931, **46**, No. 35, 2048; Page, Lubatti and Gloyns, *l.c.*). The rate of evolution of hydrogen cyanide from the discs varies with the temperature. Above 15°C. evolution is complete within 30 minutes (Page and Gloyns, J.S.C.I. 1936, **55**, 213T). Lastly, the gas may be generated *in situ* from calcium cyanide either pure or containing additional hydrogen cyanide. The powdered or granular product is exposed in thin layers on the floor. If the atmospheric humidity is more than 40% relative humidity, hydrogen cyanide is liberated by the action of water from the air. Under favourable conditions only 5% of cyanogen may remain combined after a few hours. The residue is, of course, dangerous and care must be taken to dispose of the whole of it safely (M. S. Benjamin, J. Proc. Roy. Soc., N.S.W. 1926, **60**, 38; booklet " Cyanogas Calcium Cyanide," by the American Cyanamid Co.; Miles, Bull. Ent. Res. 1928, **18**, 251; Eddy, S. Carolina Agric. Expt. Sta. 1929, Bull., No. 256; Young, Ind. Eng. Chem. 1929, **21**, 861; Dshalaganija and Iwanow, Chem. Zentr. 1938, **109**, II, 2790; Peters, Booklet, " A Short Guide to Tree Fumigation," Frankfort-on-Main, 1931; Smith, Chem. Zentr. 1937, **108**, II, 4092).

Suitability of Hydrogen Cyanide for Fumigating Various Materials.—Tea, coffee, spices, delicately flavoured nuts, etc., are liable to be spoilt. Water, watery fats, and watery and sugary foods such as milk, fruit, vegetables, both fresh and dried, minced meat, cheese and possibly other foods retain too much cyanide for raw consumption. About ten to twenty parts per million commonly remain in other products after aeration, the bulk of this being lost as a rule in cooking (Monier-Williams, Min. Health Rep. on Health and Med. Sub. 1930, No. 60). For determination a weighed sample of food is suspended in water, acidified with phosphoric or sulphuric acid and then aerated or steam distilled. The hydrogen cyanide is collected in dilute aqueous sodium hydroxide and after addition of potassium iodide and ammonia it is titrated with *N*/50 silver nitrate according to the method of Denigès (Compt. rend. 1893, **117**, 1078; Lubatti, J.S.C.I. 1935, **54**, 275T). Compounds with aldehydic or ketonic groups, such as dextrose and lævulose, may form moderately stable cyanhydrins (Monier-Williams, Min. Health Rep. on Health and Med. Sub. 1930, No. 60), and the toxicity of these compounds is not known. The rate at which they decompose is liable to be slow and independent of ordinary changes in the conditions of airing. Fumigated foods containing lævulose, in particular retain hydrogen cyanide as cyanhydrin as well as in solution, etc. The total residual hydrogen cyanide may be recovered by aerating a boiling aqueous suspension which is only slightly acid, whilst only the fumigant which is dissolved or adsorbed is recovered if the suspension is strongly acid. Thus, by pairs of determinations, the combined hydrogen cyanide is obtained by difference. The fumigation of cold stores has been successfully carried out at a mean temperature as low as 5°C. (Buttenberg, Technisches Gemeindeblatt, 1925, **28**, No. 6). Special problems of retention and aeration would seem to be involved. A survey of the literature on residual fumigants in foodstuffs, including grain and cereal products, has been made by Williams (Amer. J. Publ. Health, 1933, **23**, No. 6).

Dangers of Cyanide Fumigation.—All fumigation should be carried out by competent, trained operators. Air containing hydrogen cyanide in the proportion of one part in one hundred thousand may be breathed with impunity, one part in ten thousand is definitely dangerous, and one part in two thousand quickly produces cyanosis, a general paralysis and affection of the nervous system, and unconsciousness followed by death unless first-aid is administered at once. One part in five hundred is immediately fatal (Monier-Williams and Stock, *l.c.*; Page and Gloyns, J.S.C.I. 1936, **55**, 209T). For first-aid, *see* Military Surgeon, 1926, **59**, No. 5, 642. It is essential that a fumigated space shall be sufficiently aired before being used. The customary tests are the behaviour of white mice and the time taken to produce a standard blue colour on a filter paper freshly moistened with separate solutions of copper acetate and benzidine acetate. Other reagents are also employed (Katz and Longfellow, U.S. Bur. of Mines, Serial 2504, and J. Ind. Hyg. 1923, **5**, 27; Deckert, Z. Desinfekt. u. Gesundheitsw. 1930, **22**, 82; Oppenheim, J. Ind. Hyg. 1925, **7**, 415; Chem. Age, 1925, **13**, 474; "Methods for the Detection of Toxic Gases in Industry," H.M. Stationery Office). There is sometimes a danger of gas continuing to accumulate over a long period by desorption from fumigated goods, particularly from woollens and from bedding when this is warmed, for instance, by body heat (Kaiser, Wiener klin. Wochenschr. 1928, **41**, 958; Williams, Pests, 1938, **6**, 15 (11)). Ventilation of houses after fumigation has been studied by Page, Lubatti and Gloyns (*l.c.*) who have made recommendations for airing differently constructed houses both in winter and summer, furnished and unfurnished. The effect of heating the houses immediately after ventilation is also considered.

Addition of a Warning Gas.—This is generally a lachrymator such as a chloro- or bromo-ester, chloropicrin or cyanogen chloride. It may be of service where unskilled labour is used, but in general its value is doubtful (Pohl and Tesch, Desinfektion, 1926, **11**, 87; B.P. 271514, May 23rd, 1927; C. M. Hasselmann, Zentr. Gewerbehyg. Unfallverhüt, 1927, **16**, 65; Bellogin and Viciano, Med. paises cálidos Madrid, 1929, **2**, No. 1, 3).

Bactericidal Action.—This is very slight, *cf.* Monier-Williams (*l.c.*); *also* Fleury (Bull. Soc. Chim. Biol. 1925, **7**, 797, and Compt. rend. 1925, **92**, 596) as well as Nagel (Prakt. Desinfekt, 1927, **19**, 257).

Special Chambers, Apparatus, etc.—*See* Buildings for Fumigation of Railway Cars (Chem. and Metal, 1923, **27**, 1160); Wolters, Industrial Fumigation Chambers. (Zentr. Gewerbehyg. Unfallverhüt, 1928, **15**, 151); "Liston's Gas Disinfector," W. Glen Liston (J.S.C.I. 1925, **44**, 370). One or two British firms now manufacture fumigation chambers and equipment.

Application of Hydrogen Cyanide to the Fumigation of Ships.—The principal objective is the killing of rats which succumb far more readily than do the majority of insects and mites. The usual dose is 2 oz. hydrogen cyanide per 1,000 cu. ft., nominal concentration for at least 4 hours. Hydrogen cyanide is the most used fumigant on ships, having partly displaced sulphur dioxide on the score of efficiency and freedom from action on metals, fabrics, etc. The "pot" method of fumigation is nearly obsolete, liquid hydrogen cyanide is used chiefly in this country and America whilst "*Zyklon B*" is used principally in Germany. Zyklon has the advantage of easy regulation of dosage in small compartments, an advantage which is shared also by "discs." The chief difficulty in ship fumigation is penetration into hidden rat holes, pipe casings, propeller tunnels, dead spaces boarded up round tanks, etc., and other hiding places. Aeration is not always efficient. The actual work is trying on account of the short time available and of the cramped design of a ship's interior. The chief purpose of killing the rats is to prevent the spread of the plague flea which they carry. Cockroaches, which commonly abound, are greatly reduced in number by fumigation and a heavy dose is sometimes given to the quarters and galleys for this purpose. Occasionally ships are fumigated when laden with cargo, but hydrogen cyanide must not fall upon this (Stock and Monier-Williams, *l.c.*; Akin and Sherrard, *l.c.*; W. Heerdt, Prakt. Desinfekt. 1927, **19**, 35; "Memorandum on the Fumigation of Ships," H.M. Stationery Office, 1928; Ridlow, U.S. Publ. Health Rep., 1931, **46**, No. 28, 1623; Williams, *ibid.* 1931, **46**, No. 29, 1680, and No. 18, 1031; Symes and Roberts, Rep. Med. Res. Lab. Kenya, 1934, 20; Rev. Appl. Entomol. 1936, **24**, B, 103).

A comparison of the distribution and penetration of hydrogen cyanide and sulphur dioxide in ships has been made by Stock, Monier-Williams, Page, Lubatti and White, Bull. mens. office intern. hyg. publ. 1933, **25**, 293.

Carbon Dioxide.—This has long been used for the fumigation of grain. It is probably of value as an aid in air-tight storage in specially sound bins (W. W. Froggatt, Agric. Gaz. New South Wales, Sydney, 1921, **32**, 472; Liverpool Grain Storage and Transit Co., B.P. 429920). It is now chiefly used in admixture with other fumigants, at present mainly with ethylene oxide, when it serves two purposes, viz. the reduction of fire risk of an inflammable fumigant and the intensification of its toxic action. This last effect has been correlated with an observation by Hazelhoff (J. Econ. Entomol. 1928, **21**, 790) of the opening of the spiracles of *Periplaneta americana* in the presence of carbon dioxide. It has been observed to exert an ageing effect (Janisch, E., Arb. Biol. Reichsanst. Land-u-Forstwirts. 1924, **13**, No. 2, 173), and is used as a fore-gas in vacuum fumigation to decrease the adsorption by goods of the more toxic fumigant (E. R. (McGovran, J. Econ. Entomol. 1932, **25**, No. 2, 271; Cotton and Young, Proc. Entomol. Soc. [Wash.], 1929, **31**, No. 5, 97; R. T. Cotton, J. Econ. Entomol. 1930, **23**, No. 1, 231; Jones, *ibid.* 1935, **28**, 475).

Sulphur Dioxide—This is used mainly for the fumigation of ships for the control of rats. The toxicity has been determined by Wade (Rpt. Med. Off. Local Govt. Bd. 1903–1904 and 1905–1906; Bonjean, Rev. Hyg. 1921, **43**, 250; Clark, J. R. N. Med. Service, April, 1932). It is not highly toxic to insects, but is still fairly extensively used to kill bedbugs. Its chief advantages are safety and cheapness. It is usually generated *in situ* by burning sulphur in iron pans, or carbon disulphide by a patented method. About 10% sulphur trioxide is produced by burning sulphur (Lubatti, J.S.C.I. 1936, **55**, 344T). Its chief value is as a warning agent. Sulphur dioxide seriously affects many substances, *e.g.* wool and most textiles which are reduced in strength and dyed material which is often partly bleached. The germination of grain is seriously reduced. The baking strength of flour is greatly reduced and fresh and dried foods are mostly spoilt. All the common metals are attacked. Sulphur trioxide is even more destructive. In the Clayton process (Pacha, Bull. mens. office intern. hyg. publ. 1933, **25**, 1358) the sulphur is burnt in a special apparatus which is brought alongside the ship, air drawn from the holds being passed over it and returned by a system of pipes and blowers. The nominal dose, prescribed by different countries for the control of rats in ships varies from 40–60 oz. per 1,000 cu. ft., the time of exposure from 1–8 hours (Stock, Bull. mens. office intern. hyg. publ. 1933, May session; Wade, *l.c.*; Williams, U.S. Publ. Health Rep. 1934, **48**, 89; Stock, Monier-Williams, Page, Lubatti and White, *l.c.*). Sulphur dioxide is still extensively used as a bactericide. *B. anthracis* is particularly resistant to it (Wade, *l.c.*; Trembur. Arch. Hyg. 1905, **52**, 255; Croner, "Lehrbuch der Desinfektion," 1913; Rideal and Rideal, "Chemical Disinfection and Sterilisation," 1921).

Ethylene Oxide.—This important fumigant is stored and transported in steel cylinders as a liquid, b.p. 10·5°. It is used in three ways, either by being sprayed through a short bifurcated copper tube, the carbon dioxide with which it is mixed assisting to expel it from the cylinder, or by vaporising it in a suitable vaporiser, or by mixing the liquid with the requisite amount of solid carbon dioxide, the resulting slush being used mainly for the fumigation of grain with which it is fed automatically or by shovelling into the silo bin or elevator.

A suitable vaporiser is described by Page and Lubatti (J.S.C.I. 1935, **54**, 246T). This comprises spray jets and deflectors for spreading the liquid over a corrugated heat-exchange surface placed in a water bath which is heated by immersion heaters. After passing through a mist trap, in which the temperature of the gas is raised, it is led to the fumigation chamber through a thick-walled rubber hose. The average lethal dose for most insects is roughly three times that of hydrogen cyanide. Certain insects are, however, relatively more susceptible to ethylene oxide, *e.g.* *Calandra* spp. It is a very effective ovicide and is much less toxic to man than is hydrogen cyanide, an overdose produces nausea and vomiting which generally lasts about 8–10 hours. The pure gas is colourless and odourless, but commercial preparations, which are generally about 97–98% pure, have a characteristic ethereal-aldehydic odour. This is not very powerful and is not a reliable guide to the concentration after airing. Smarting or tingling of the eyes is produced by concentrations of 15 mg. per litre or more. Short spells of work may be undertaken in concentrations of 1–2 mg. per litre. According to Fleury (Verhandl. deut. Path. Ges. 1930, **10**, 4) a concentration of 1 mg. per litre is dangerous, but 0·5 mg. per litre can readily be endured for 1 hour. In Germany houses fumigated with ethylene oxide must be ventilated for at least 6 hours and the residual concentration must not be more than 0·5 mg. per litre (Reichsgesundheitsblatt, 1935, No. 3, 45; Chem. and Ind. 1935, **58**, 16). Precautions to be taken when fumigating with ethylene oxide are described by Walker and Greeson (J. Hygiene, 1939, **32**, 409). The inflammability, which is comparable with that of acetylene, has been determined by Jones and Kennedy (Ind. Eng. Chem. 1930, **22**, 146) and by Deckert (Zentr. Gewerbehyg. Unfallverhüt, 1931, **18**, 28). Complete freedom from fire risk necessitates dilution with more than seven times the amount of carbon dioxide; mixtures containing only 10% carbon dioxide, however, are non-inflammable at the concentrations obtaining during practical fumigation except during a short initial period. Ethylene oxide and carbon dioxide have the same molecular weight and do not separate in the fumigation chamber. Two mixtures are in common use, the German "*Aetox*" or "*T-Gas*" containing 10% carbon dioxide and a mixture known as "*Cartox*" in Germany and as "*Carboxide*" in America containing 90% carbon dioxide. This is used chiefly for the fumigation of grain (Tesch, Z. hyg. Zool. Schädlingsbekämpf. 1937, **29**, 244). The distribution of ethylene oxide in large spaces has been studied by Page and Lubatti (J.S.C.I. 1933, **52**, 309T). They found a marked layering near the floor owing to cooling of the air by the spray. This was overcome by vaporising the liquid by heat and by stirring the air. The distribution in barges containing dried fruit in boxes has been studied by Burns Brown (J.S.C.I. 1937, **56**, 116T). With suitable stacking even distribution was readily obtained. In order to ensure satisfactory concentrations near the hatch covers it was necessary to release the gas at several points in close proximity to them.

Suitability of Ethylene Oxide for Fumigating Various Materials.—The flavour of ham, chocolate and cocoa has been stated to have been impaired, but reports to the contrary have also been made. Probably purity of the oxide is the determining factor. Some foods, such as nutmeats, absorb large quantities of the gas, as also do watery foods. It softens lacquer and seriously reduces the percentage germination of most seed. Some of the oxide absorbed is converted into glycol or like compounds the physiological action of which may be expected to be slight (Browning, "Toxicity of Industrial Organic Solvents," H.M. Stationery Office, 1937, p. 333). Ethylene oxide must be used with caution, however, on all viable matter. It is used more for dried fruit, nuts and grain than for other products, although stored apples and potatoes are treated with it (Vayssière, Compt. rend. Acad. Agric. France, 1936, **22**, 934), and it is said to be suitable for meats and dairy products (Austr. Food Manufac. 1935, **5**, 5). It is used in Germany against bed-bugs (Hase, Z. hyg. Zool. Schädlingsbekämpf, 1937, **29**, 65; Tesch, Z. Gesundheitstech. u. Städtehyg. 1933, **25**, 326), and in Germany and the U.S.A. for killing insects as well as rats in ships (Brown, U.S. Naval Med. Bull. 1934, **32**, 294; Schwartz and Deckert, Z. Desinfekt. u. Gesundheitsw. 1931, **23**, 405). The reagent used for absorbing ethylene oxide, whether this be drawn from the air space or driven out of fumigated products by aeration (Sudendorf and Kröger, Chem.-Ztg. 1931, **55**, 569), is a standard solution of hydrochloric acid saturated with sodium chloride (Deckert, Z. anal. Chem. 1930, **82**, 297), or, better, with magnesium chloride (Lubatti, J.S.C.I. 1932, **51**, 361T) or magnesium bromide (*idem. ibid.* 1935, **54**, 424T). Chlorohydrin is formed and the excess acid is titrated; *see also* Kerckow, Z. anal. Chem. 1937, **108**, 249; Deckert, Angew. Chem. 1932, **45**, 559. General references: Young and Busbey, Pub. Div. Insecticide Invest. Washington D.C. Bur. Entomol. Plant Quarantine, April, 1935; Potter, Ann. Appl. Biol. 1937, **24**, 415; MacBride, Chem. Zentr. 1936, I, 416; Shepard, Lindgren and Thomas, Minnesota Agric. Exp. Sta. Tech. Bull., No. 120, 1937.

Carbon Disulphide.—This is one of the oldest fumigants and is still largely used, particularly in remote parts, where its ease of transport and of application are a great advantage. It is applied either by sprinkling or spraying over the goods to be fumigated, or by pouring into shallow pans placed at the top of the chamber. Either method is satisfactory. The chamber must be air-tight and the temperature not below 70°F. Better results are obtained, especially in cold weather, by using a heated vaporiser such as that described by Weigel, Young and Swanson (U.S. Dept. Agric. 1927, Circular No. 7). Carbon disulphide is cheap so that a heavy dose may be given up to 10 or 15 lb. per 1,000 cu. ft. It is moderately toxic to man, and the vapour should be breathed as little as possible (Browning, "Toxicity of Industrial Organic Solvents," H.M. Stationery Office, 1937, p. 361). In air-tight containers filled with grain or like material the penetration is said to be excellent owing to the displacement upwards of the inter-granular air by the heavy vapour; allowance must be made for absorption on the grain.

Inflammability.—Carbon disulphide is highly inflammable and has a very low flash-point and ignition temperature. It is never used in buildings without the addition of a large proportion of carbon tetrachloride to lessen the fire risk. This mixture, however, is a poor fumigant and owing to the different partial pressures of the constituents and the different densities of their vapours it is prone to change in composition and to give non-toxic or inflammable fractions. One prominent feature of carbon disulphide is its ineffectiveness against eggs, another is its anæsthetic effect on other stages (Hamlin and Reed, J. Econ. Entomol. 1927, **20**, 400, and 1928, **21**, 783). It is suited to the fumigation of damp or viable produce such as seeds or potatoes but cannot be used with any fatty material.

Determination.—Carbon disulphide in foodstuffs may be detected by the sensitive reactions of Perkins (Pharm. J. 1924, **113**, 101 and 131), Malowan (Parfümeur, 1930, **4**, 21), Feigl and Weissenberg (Z. anal. Chem. 1931, **83**, 93), and Tischler (Ind. Eng. Chem. [Anal.], 1932, **4**, 146). It may be determined in alcoholic solution by distillation or aeration, absorption in alcoholic potash which converts it into the xanthate and oxidation to sulphate by bromine (Spielmann and Butler Jones, J.S.C.I. 1919, **38**, 185T; Huft, J. Amer. Chem. Soc. 1926, **48**, 81; Matuszak, Ind. Eng. Chem. [Anal.], 1932, **4**, 98; Marsh and Cruess, Fruit Products and Amer. Vinegar Ind. 1929, **8**, No. 6, 31; Komar and Maevskaja, J. Appl. Chem. Russia, 1934, **7**, 433; Higgins and Pollard, J.S.C.I. 1937, **56**, 122T). Mixtures with carbon tetrachloride may be analysed by the method of Warren (Amer. J. Pharm. 1923, **95**, 864) or by that of Spausta (Motorenbetrieb. u. Maschinen-Schmierung, 1930, **7**, 7). General references: M. R. Osburn, N.J. Dept. Agric. 1930, Circular, No. 188 (Fresh Fruit); Sanders and Wahl, Union S. Africa Dept. Agric. 1927, Bull., No. 28 (Maize); Wenholz, Agric. Gaz. New South Wales, 1927, **38**, 255 and 367 (Maize); Jancke and Lange, Z. angew. Entomol. 1930, **17**, No. 2, 386 (Herbarium Plants); Vichamco, Philippine Agric. 1932, **20**, No. 9, 593 (Timber); Larson, J. Agric. Res. 1924, **28**, 347 (Beans); K. Endo, Kontyû, 1937, **11**, 70; and Rev. Appl. Entomol. 1937, **25A**, 335 (Wheat).

The Halogenated Hydrocarbons.—Carbon tetrachloride, trichlorethylene and ethylene dichloride are fumigants of some importance. The order given is that of increasing inflammability; ethylene dichloride is barely inflammable, carbon tetrachloride is a good fire extinguisher. They require a temperature of 70°F. or over to be really effective unless a heated vaporiser is used, and their vapours are all much heavier than air. Carbon tetrachloride, which is commonly used with carbon disulphide, may be replaced by trichlorethylene. Ethylene dichloride is by far the most toxic. It is used to some extent, mixed with carbon tetrachloride in the ratio of 3:1 by volume, for the fumigation of grain and of furniture and other goods in special chambers some of which are heated. A combination with trichlorethylene is useful since a mixture can be selected, the partial vapour pressures of the constituents of which are equal. There is also the advantage of the greater toxicity of trichlorethylene.

Pentachlorethane is a constituent of a spray-cum-fumigant used in the disinfection and disinfestation of rolling stock (L. F. Hoyte, Ind. Eng. Chem. 1928, **20**, 460 and 931; J. E. Thomas, J. Counc. Sci. Ind. Res. Australia, 1929, **2**, 128). These compounds do not much reduce the percentage germination of grain (A. Müller, Chem.-Ztg. 1927, **51**, 510). If pure they have little action on metals (Formánek, Chem. Zentr. 1930, **101**, II, 976). They are definitely poisonous (Browning, "Toxicity of Industrial Organic Solvents," H.M. Stationery Office, 1937, 136).

Trichlorethylene is used as a seed disinfestant (Bouhelier and Fouvy, Rev. Path. vég. 1938, **25**, 5).

Experiments have been conducted by a few workers on *methallyl chloride*, $CH_2:CMe{\cdot}CH_2Cl$ (Briejèr, Nature, 1938, **141**, 1099; "Methallyl Chloride as a Fumigant against Insects infesting Stored Products," N. V. de Bataafsche Petroleum Maatschappij).

Methyl Bromide has been widely tested and found to be very effective, but its use on a large scale so far has been restricted owing to its toxicity to man. While there is no doubt that this is high it need not prove an insuperable drawback. The evidence at present is somewhat conflicting (Mackie, J. Econ. Entomol. 1938, **31**, 70; Fiske and Shepard, *ibid.* 1938, **31**, 79; Munro, Rep. Entomol. Soc. Ont. 1938, **68**, 72). Methyl bromide is non-inflammable and has been used to reduce fire risk of ethylene oxide (Le Goupil, Rev. Path. vég. 1932, **19**, 169).

para-*Dichlorbenzene* is used as a fumigant against clothes moth (Suter, Swiss P. 201548), against wood-boring beetles and against potato weevils, *Cyclas formicarius* (U.S. Dept. Agri., Leaflet No. 121). For use against wood-boring beetles the *p*-dichlorbenzene is dissolved, sometimes in *o*-dichlorbenzene, and sprayed or applied to the woodwork with a brush, after which the holes should preferably be filled with bees-wax or covered with pasted paper.

o-Dichlorbenzene was used fairly extensively for bed-bug fumigation in houses. This practice is now deprecated by the Ministry of Health which has advised local authorities against it pending further investigations on its toxicity to man. It appears to have a cumulative toxic effect at low concentrations and long periods of exposure; houses fumigated with it could not be aired sufficiently rapidly (Cameron and Thomas, J. Path. Bact. 1937, **44**, 281).

Chloropicrin is a fumigant with a fairly high toxicity. Its use is limited by its corrosive action on metals, its destruction of yeast activity, its bleaching of flour, and other disadvantages (Chapman and Johnson, J. Agric. Res. 1925, **31**, 745). It is a powerful lachrymator, is poisonous and its effects are probably cumulative, some persons being peculiarly sensitive. It is quite widely used, although not in this country. It is applied by spraying under pressure, as in the machinery piping system for flour mills described by Dean, Cotton and Wagner (U.S. Dept. Agric. 1936, Circular No. 390). It is also sprinkled over goods or ladled into milling or other machinery. It is also used in chambers equipped with vaporising, gas circulating and heating devices. It is very slightly soluble in water by which it is not hydrolysed. Its vapour is stated not to be strongly absorbed by fibrous materials although it is readily held by active charcoal (Herbst, Biochem. Z. 1921, **115**, 204). It is said to have an irritant action at a concentration of 0·02 mg. per litre (Kiss, Z. ges. Schiess- u. Sprengstoffw. 1930, **25**, 260 and 300). According to Deckert (Z. Hyg. Infektionskrankh. 1929, **109**, 485) this physiological detection is more sensitive than any of the chemical tests. The principal chemical tests are those of Nekrassov (Voina i Tecnica, 1926, **275**, 32) in which a yellow precipitate is formed by passing the gas through an alcoholic solution of the potassium salt of dithioethylene glycol; and of Deckert (Z. anal. Chem. 1938, **113**, 183) in which dimethylaniline paper changes from white to yellow or maroon in presence of the gas. The first reaction may be used for determination since potassium chloride is formed quantitatively. The lachrymatory property of chloropicrin should be a safeguard in its use. The limit of supportability is said to be 0·05 mg. per litre whilst the lethal exposure time at a concentration of 1·0 mg. per litre is said to be 20 minutes (Prentiss, "Chemicals in War," New York, 1937). General references.—Grain: Harukawa and Kumashiro, Ber. Ohara Inst. 1934, **6**, 407; Bertrand, Chim. et Ind. 1937, **37**, 419. Rice: Kono, J. Plant Prot. 1937, **24**, 520. Bed-bugs: Gounelle and Roul, Rev. Service Sant. Milit. 1937, **106**, 881. Tobacco: Skalov, Tobacco Ind. 1934, No. 1, 20. Rats: Piedallu, Bull. mens. office intern. hyg. publ. 1930, **22**, 763; Johnson, Sanit. Products, Sect. Soap, 1935, **11**, 105, 107, 109. Bacteria: Violle, Compt rend. 1926, **182**, 290. Elimination after fumigation: Jefimenko, Chem. Zentr. 1937, **108**, II, 2035. Bibliography: Roark and Busbey, U.S. Dept. Agric. Bur. Entomol. Plant Quarantine, 1935, E-351; Expt. Sta. Rec. 1935, **73**, 647).

Other Fumigants.—*Ethyl* and *methyl formates* are used, chiefly in the fumigation of packed goods, *e.g.* dried fruits (Co-operated Dried Fruits Sales Pty. Ltd., Chem. Zentr. 1936, **107**, I, 1935). When these are used on a larger scale, *e.g.* in milling machinery, a large proportion of carbon dioxide is added to reduce inflammability.

Phosphine, generated by the action of moisture from the air on aluminium or calcium phosphide contained in packets, is used in Germany, chiefly for the fumigation of bulked grain. The packets are buried in the grain which is exposed to a low concentration for a long period (Mayer, Z. Gesundheitstech. Städtehyg. 1934, **26**, 377; Freyberg, Chem. Zentr. 1937, **108**, II, 125). The poisonous nature of the gas is stressed by Flury (Anz. Schädlingskunde, 1937, **13**, 26).

Hydrogen Sulphide is used principally in Russia, against rats (Krylova, Bull. Plant Protection, U.S.S.R. 1935, **6**, Ser. 3, 68; Amer. Chem. Abs. 1937, **31**, 2342); as a seed disinfectant (Vzoroff, Bull. Plant Protection, Leningrad, 1935, **6**, Ser. 3, 48; Rev. App. Myc. 1936, **15**, 669); for grain and vegetables (Edelman, Lenin Acad. Agric. Sci. 1936, 422; Rev. Applied Entomol. 1937, **25A**, 158).

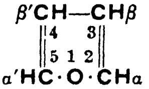
A fraction of heavy *coal tar naphtha* with a boiling range of about 150–180°C. is now being used in England for the fumigation of empty buildings, chiefly houses infested with bed-bugs (Ashmore and McK. Hughes, Brit. Med. J. 1937, i, 459; Cameron, J. Path. Bact. 1938, **46**, 95). The proportion of low boiling constituents is governed by the flash point, a certain proportion of unsaturated heterocyclic compounds should be present as well as a proportion of paraffins, of which the cyclic paraffins are the more toxic, and a small proportion of cresols.

The following is a short list of papers dealing with practical methods of fumigation in Germany and America and with the suitability of different fumigants for various products:—Back and Cotton, U.S. Dept. Agric. 1935, Circ. P. 3638, 369; Peters, Chem. Zentr. 1938, **109**, I, 703; Anz. Schädlingskunde, 1938, **14**, 116; Gassner, Z. hyg. Zool. Schädlingsbekämpf. 1937, **29**, 176. Dried fruit: Simmons, U.S. Dept. Agric. Bur. Entomol. Plant Quarantine, 1935, E-**353**, 15; Amer. Chem. Abs. 1936, **30**, 8418. Bed-bugs: Gunderson and Strand, J. Econ. Entomol. 1939, **32**, 106. Grain and flour: Shepard, Minn. Agric. Expt. Stat. Tech. Bull. 1937, **120**, 3; Amer. Chem. Abs. 1937, **31**, 7185.

A. B. P. P.

FUNGISTEROL (*v.* Vol. IV, 331*c*).

FURAN. [Furfuran]



Furan is a five membered heterocylic ring containing four carbons and one oxygen. It was first obtained by Rohde and is described by Limpricht (Ber. 1870, **3**, 90) under the name of *Tetraphenol.* Derivatives of furan were known as far back as 1780 when Scheele first obtained α-furoic acid (pyromucic acid) by pyrolysis of mucic acid. Furfural, the α-aldehyde of furan, was discovered by Döbereiner (Annalen, 1832, **3**, 141).

Furan occurs in the wood oil obtained by the distillation of resinous woods such as Pine (Atterberg, Ber. 1880, **13**, 879). It is a constituent of Finnish oil of turpentine (Aschan, Z. angew. Chem. 1907, **20**, 1813). Furan has been obtained by heating succindialdehyde with water in a sealed tube at 180° (Harries, Ber. 1901, **34**, 1496); by the distillation of calcium succinate (Metzner and Vorländer, Ber. 1898, **31**, 1886); by distillation of 2:5-dihydrofuran with phosphorus pentachloride (Henninger, Ann. Chim. Phys. 1886, [vi], **7**, 220); by distillation of the barium salt of pyromucic acid with soda lime (Limpricht, Annalen, 1873, **165**, 281); apparently by passing acetylene and steam over aluminium oxide at 400–425°; and together with other products by passing acetaldehyde or paraldehyde over heated Al_2O_3 (Tschitschibabin, Chem. Zentr. 1916, I, 920).

Furan is obtained in moderate yield when furfural vapours are passed through soda lime at 350° (Hurd and Osborne, J. Amer. Chem. Soc. 1932, **54**, 2532).

Preparation.—Furan has been prepared by heating pyromucic acid (furan-2-carboxylic acid, α-furoic acid) in a sealed tube for 2 hours at 200–275° (Freundler, Compt. rend. 1897, **124**, 1157).

An improved method of preparation is given in "Organic Syntheses" Collective Vol. I, p. 269; the furan-2-carboxylic acid is distilled from round bottom flask which is fitted with an upright tube 2·5 cm. in diam. and 15 cm. long provided with a side arm of the same diameter about 2 cm. from the top. The side arm extends into the bottom of an efficient 25 cm. soda lime tower immersed in water at 40° to prevent condensation of furan. From the top of the tower an outlet tube 5 cm. in diam. is extended to the top of an upright water condenser, to the lower end of which is attached a receiving flask surrounded by ice and salt. The top of the upright tube in the reaction flask is closed by a cork stopper holding a glass rod for pushing back any sublimed acid into the flask. The acid is heated to its boiling-point, 200–205°, when furan and CO_2 are evolved. The furan is redistilled, b.p. 31–34°/745 mm., yield 78%.

The above method has the disadvantage that it is necessary to push back sublimed α-furoic acid in order to avoid clogging and to obtain a more complete conversion of the acid into furan. H. Gilman and M. Lousinian (Rec. trav. chim. 1933, **52**, 156) have found that the decarboxylation of α-furoic acid may be effected with 90% yield if crude tar bases are used as solvent with small quantities of $CuSO_4$ or CuO as catalyst.

A further improvement has been made by E. Wagner and J. Simons (J. Chem. Educ. 1936, **13**, 265) using CuO as catalyst but substituting quinoline for the crude tar bases. The CuO is reduced to Cu and can be used repeatedly with the same quinoline without loss of efficiency.

Constitution.—A satisfactory formula should take into account.

(1) The tendency of furan to form oxonium compounds (Gilman and Wright, J. Amer. Chem. Soc. 1930, **52**, 3349).

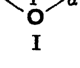
(2) The super-aromatic properties of the furyl radicle (*see* p. 399*d*), exceeding those of phenyl and thienyl (Gilman and Towne, Rec. trav. chim. 1932, **51**, 1054).

(3) The highly chromophoric properties of the nucleus (Stobbe and Eckert, Ber. 1905, **38**, 4074).

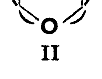
(4) Marked tendency for α- substitution.

(5) Apparent conjugated system that underlies 1:4-addition (Gilman and Wright, *l.c.*).

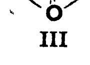
The following formulæ have been suggested:



I

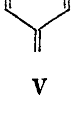


II

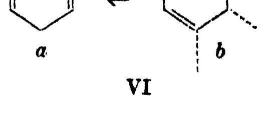


III

IV



V



VI

I is the form in general use to-day and was suggested by Baeyer and Emmerling (Ber. 1870, **3**, 517; Marchwald, *ibid.* 1888, **21**, 1401).

Since the distribution of the fourth valency of each C-atom is unknown, formulæ II (Steinkopf *et al.*, Annalen, 1921, **424**, 61; 1922, **430**, 78), III (Hughes and Johnson, J. Amer. Chem. Soc. 1931, **53**, 737) and IV (Baeyer, Ber. 1877, **10**, 1358) have been suggested by analogy with benzene.

V has been suggested by Gilman and Dickey (Iowa State Coll. J. Sci. 1932, **6**, 381), and VI is a modification of the Kekulé revised formula for benzene, *b* being the active form.

Gilman, Burtner and R. Vanderwal (Rec. trav. chim. 1933, **52**, 151) have demonstrated the equivalence of the two α and also of the two β positions; thus VI*b* is not now feasible.

Electronic formulæ for the furan ring are discussed in a paper by E. Hughes and J. Johnson (*l.c.*).

PHYSICAL PROPERTIES.—Furan is a colourless liquid which may be solidified by rapid evaporation (Limpricht, *l.c.*), b.p. 31·4–31·6°/756 mm.; (Henninger, *l.c.*), d^{0} 0·9626; $d^{19\cdot7}$ 0·938, $n_{D}^{20\cdot3}$ 1·4214 (Landrieu, Baylocq, Johnson, Bull. Soc. chim. 1929, [v], **45**, 36).

Heat of vaporisation 95·50 g.-cals. at 31·2° (Mathews and Fehlandt, *ibid.* 1931, **53**, 3212).

Specific heat C_p (molal) of furan is given by $14\cdot2341+7\cdot188\times10^{-2}t-1\cdot071\times10^{-4}t^{2}$ (Jennings and Bixler, J. Physical Chem. 1934, **38**, 747).

Furan is insoluble in water, easily soluble in alcohol and ether, the vapour is quantitatively absorbed by 82·5% H_2SO_4 and this method may be used for the separation from ethylene but not from other unsaturated hydrocarbons (Hurd and Goldsby, J. Amer. Chem. Soc. 1932, **54**, 2558).

Furan and simple derivatives exhibit no selective absorption in the visible or ultra-violet regions (to 2200Å). Molecular absorption coefficients are, however, consistently higher for α- than for β-derivatives and give a means of distinction (Hughes and Johnson, *l.c.*).

CHEMICAL PROPERTIES.—Furan decomposes at 670–740° in a quartz tube without a catalyst as contrasted with a temperature of 360° when heated in the presence of a nickel catalyst. The products at 670° are CO 75%, saturated hydrocarbons and hydrogen 12%, unsaturated hydrocarbons 13% (acetylenes; C_2H_4; C_3H_6, allene, *cyclo*propene and butadiene) (Hurd and Goldsby, *l.c.*).

Furan and certain of its derivatives resinify with mineral acids, thus rendering nuclear substitution difficult (Limpricht, Ber. 1870, **3**, 90); but many negatively substituted furan derivatives are stable towards acids (including halogen acids), Gilman and Young (Rec. trav. chim. 1932, **51**, 761).

Metallic sodium and alkalis do not attack furan and it combines neither with bisulphite nor hydroxylamine.

Reduction.—Reduction with hydrogen in the presence of nickel at 170° gives tetrahydrofuran, b.p. 64–65°/760 mm. together with *n*-butyl alcohol and other products (Bourguignon, Chem. Zentr. 1908, **I**, 1630).

Catalytic reduction using PdO gives 93–6% tetrahydrofuran (Starr and Hixon, Organic Syntheses, 1936, **16**, 17–80). 2:5-Dihydrofuran is known but has not been prepared by hydrogenation.

Oxidation.—Peracetic acid mainly polymerises furan but one of the products obtained in small yield forms a hydrazone.

Perbenzoic acid in chloroform gives a benzoate of 1:2-dihydroxy-1:2-dihydrofuran, m.p. 98–100° (Böeseken, Vermji, Bunge and van Meeuwen, Rec. trav. chim. 1931, **50**, 1023).

Vanandium pentoxide at 250–410° with air or oxygen yields 65% maleic acid (N. Milas and W. Walsh, J. Amer. Chem. Soc. 1935, **57**, 1389).

The *Liebermann-Burchard* reaction applies also to furan and many of its derivatives: 1–2 drops of solution or 10–20 mg. of solid dissolved in 2 c.c. chloroform, 10 drops of $(CH_3CO)_2O$ and 1–3 drops of conc. H_2SO_4 added (Levine and Richman, Proc. Soc. Exp. Biol. Med. 1934, **31**, 582). The pine splinter reaction (pine chip moistened with HCl) used for the pyrrole ring is also applicable to furan and most of its compounds. The monosubstituted furans give a green colour, but the high melting furans give a red colour similar to that given by pyrrole compounds. The Ehrlich test for the pyrrole ring (6-dimethylaminobenzaldehyde) is also given by the high melting furans (Reichstein, Helv. Chim. Acta, 1932, **15**, 1110).

Nitration.—By treatment of furan with fuming nitric acid in acetic anhydride, 5-nitro-2-acetoxy-2:5-dihydrofuran is obtained (Marquis, Compt. rend. 1902, **134**, 776; Johnson, J. Amer. Chem. Soc. 1931, **53**, 1142). The nitro group markedly increases the stability of furan (Gilman and Wright, *ibid.* 1930, **52**, 2550).

Sulphonation.—Furan has not yet been sulphonated but 2-furansulphonic acid and its derivatives have been prepared by indirect methods.

Ice-cold furan in chloroform treated with ozone diluted with CO_2 gives a resin on evaporation which on treatment with water leaves a maroon-coloured compound of formula $C_{12}H_{12}O_{10}$, soluble in cold 10% NaOH and glacial acetic acid, and gives the characteristic reaction with a pine splinter. The ozonide of furan is so unstable (decomposition above 0°) that it could not be isolated (M. Freri, Gazzetta, 1933, **63**, 281).

Gilman and Breuer have succeeded in obtaining metallic derivatives of furan, *e.g.* 2-furylsodium (J. Amer. Chem. Soc. 1934, **56**, 1123).

The Friedel-Crafts reaction has been frequently applied in furan chemistry for nuclear substitution (Gilman and Calloway, *ibid.* 1933, **55**, 4197; McCorkle, Gilman and Calloway, *ibid.* 1934, **56**, 745).

Furan reacts with dry HCN and HCl (Gatterman reaction) except when both α-positions are occupied or when the —COOR or phenylene groups replace H in the ring (T. Reichstein, Helv. Chim. Acta, 1930, **13**, 349, 1930).

Aromatic Properties.—Super-aromatic properties are ascribed to a compound when it undergoes a typical aromatic reaction more readily than the parent unsubstituted compound. Like thiophen, furan, and especially the α-substituted furans, possess super-aromatic properties. The β-substituted furans are less aromatic but appear to exceed the benzene types which they otherwise resemble closely. The results show that 2-furyl, 2-thienyl and phenyl are decreasingly aromatic (Gilman and Towne, Rec. trav. chim. 1932, **51**, 1054; Gilman and Calloway, J. Amer. Chem. Soc. 1933, **55**, 4197; Gilman and Young, *ibid.* 1934, **56**, 464).

Orientation.—(1) Direct nuclear substitution of furan gives an α-mono-substituted furan and no β-substituted isomer is formed.

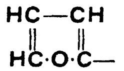
(2) Direct nuclear substitution of an α-substituted furan gives an αα′-disubstituted furan, apparently to the exclusion of any isomeric αβ-disubstituted furan.

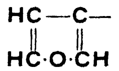
(3) Direct nuclear substitution of an αα′-disubstituted furan yields generally but one αα′β-trisubstituted furan. If in an αα′-disubstituted furan one of the substituents is an *o*-*p*-director in benzene and the other a *m*-director the entering element or group is directed to that β-position contiguous to the *o*-*p*-director (Gilman, Calloway and Smith, *ibid.* 1934, **56**, 220).

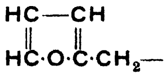
(4) Direct nuclear substitution of β-substituted furans, now available by indirect methods, involves the replacement of an α-hydrogen. If the β-group is an *o*-*p*-director in the benzene series the entering group goes to the contiguous α-C atom, if a *m*-director to the more remote or opposite α-C atom (Gilman and Burtner, *ibid.* 1933, **55**, 2903).

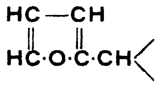
See also Gilman and Wright, Chem. Review, 1932, **11**, 323; Gilman *et al,* "Orientation in the Furan Nucleus," J. Amer. Chem. Soc. 1932, onwards.

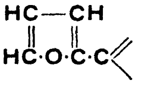
DERIVATIVES.—Nomenclature:

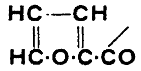

α-Furyl or Furyl-2.


β-Furyl or Furyl-3.


Furfuryl.


Furfuryliden.


Furfurenyl.


Furfuroyl (Pyromucyl).

The following are a few of the more important compounds:

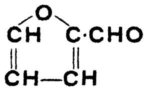
Furfural (*q.v.*).

Sylvan or 2-methylfuran is obtained from the distillation of wood oils, b.p. 65°/759 mm. (Harries, Ber. 1898, **31**, 37).

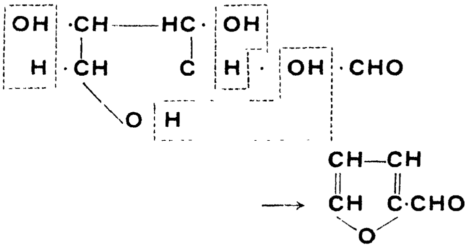
Ethylfuran, b.p. 91·3° (Paul, Bull. Soc. chim. 1935, [v], **2**, 2220).

Furfuryl alcohol, liquid with a characteristic odour, b.p. 68–69°/10 mm., b.p. 170–171°/758 mm. (Erdmann, Ber. 1902, **35**, 1855). Furfuryl alcohol is used in the manufacture of resins and textile dyes.

FURFURAL (furfurol, furfuraldehyde, 2-furaldehyde, pyromucic aldehyde),



is formed in small yield in a wide variety of organic decompositions, such as the distillation of oak timber, the fermentation of carbohydrates, and from sugar by the action of sulphuric acid and manganese dioxide (Döbereiner, 1830), but the only practical method of preparation is the dehydration of pentoses (or pentosans, which give pentoses on hydrolysis) by boiling with dilute HCl or H_2SO_4 (Pervier and Gortner, Ind. Eng. Chem. 1923, **15**, 1167, 1255). The furfural distils off in steam. The reaction proceeds thus:



(Tollens and Stone, Annalen, 1888, **249**, 227). Pentosans are present in all naturally occurring cellulosic materials such as wood, straw, bran and grain hulls. Oat hulls are a very fruitful source, containing 32–36% of pentosans, and have been utilised by the Quaker Oats Co., Ltd., for the large scale preparation of furfural *see* Miner and Brownlee, U.S.P. 1735084. The hulls, moistened with 5% sulphuric acid, are hydrolysed at 150° by a current of steam at 60 lb. pressure in rotary steel autoclaves. The furfural is recovered by fractionation. For high yields, a small water–hull ratio is essential, the best yield (10% on the weight of the hulls) being obtained when the ratio is 0·27 (Brownlee, Ind. Eng. Chem. 1927, **19**, 422).

Pure furfural is a colourless liquid miscible with most organic solvents except petroleum hydrocarbons and glycerol. Mains (Chem. Met. Eng. 1921, **26**, 779, 841) gives: b.p. 161·7°/760 mm., f.p. −36·5°, d_4^{20} 1·1598, d_4^{25} 1·1545.

	20° %	30° %	90° %
Solubility of furfural in water	8·3	8·8	16·6
Solubility of water in furfural	4·8	5·8	13·5

Mains also gives densities, boiling-points and distillation composition of various water–furfural mixtures. Evans and Aylesworth (Ind. Eng. Chem. 1926, **18**, 24) give n_D^{20} 1·52608, b.p. 161·7°/760 mm. They also give the vapour-pressure curve from 40–170°, *i.e.* 8 to 966 mm. Berthelot and Rivals (Compt. rend. 1895, **120**, 1086) give the heat of formation as 49·7 kg.-cal., The flash point 55–57°. Mathews (J. Amer. Chem. Soc. 1926, **48**, 562) gives the heat of vaporisation as 107·51 g.-cal.

For the detection of furfural Tollens reagent (orcinol in HCl) is most sensitive, giving a red colour with 1 part in 600,000 (Justin-Mueller, J. Pharm. Chim. 1921, [vii], **24**, 334). The use of aniline (Tolman and Trescot, J. Amer. Chem. Soc. 1906, **28**, 1629) or xylidene (Suminokura and Nakahara, 1929, A, 86) in place of the orcinol are recommended. The test with orcinol has been extended to a colorimetric method of estimation by Fleury and Poirot (J. Pharm. Chim. 1922, [vii], **26**, 87).

Three methods of estimation are in use:

(1) Reaction with hydroxylamine hydrochloride and titration of the HCl liberated by the formation of the oxime (Noll, Bolz and Belz, Papier-Fabr. 1930, **28**, ii, 568).

(2) Precipitation with phloroglucinol in HCl (Kröber *et al.*, Z. angew. Chem. 1902, **15**, 477).

(3) Pervier and Gortner have reviewed all previous methods and devised a method of electrometric titration with potassium bromate (Ind. Eng. Chem. 1923, **15**, 1167, 1255). For the occurrence and estimation of furfural in foodstuffs, *see* papers by Lampitt *et al.* in the Analyst, 1927–31.

Although furfural has only been a commercial product since 1923, it and its numerous derivatives have found wide application in industry and offer promise of considerably increased usefulness. As a *selective solvent* it is used in the purification of lubricating oils (Bryant, Manley and McCarty, Oil and Gas J. 1935, **33**, 50) and of pine resin (Kaiser and Hancock, Ind. Eng. Chem. 1930, **22**, 446), and in the extraction of impurities from oils and fats (Tischer, U.S.P. 2090738). Among numerous minor uses as a *solvent* may be mentioned its use in the grinding wheel industry, when it is used as a solvent for the binder (Brock, U.S.P. 1537454), for cellulose nitrate (Trickey, Ind. Eng. Chem. 1927, **19**, 643) and in the shoe dyeing industry, where its great penetrating power and relatively non-toxic character make it an ideal solvent (Miner, U.S.P. 1760076). A recent patent suggests its use in the manufacture of crease-resisting cloth (B.P. 445243).

It has found use as a *wetting agent* to prevent efflorescence on silica films and bubbles on electrotype plates.

It is important in the manufacture of *synthetic resins*. It combines readily with phenols to give potential resins, which when heated under pressure with an accelerator give excellent mouldings (Novotny, U.S.P. 1398146; Peters, Ind. Eng. Chem. 1936, **28**, 755).

Similar condensations occur with amides (Cherry and Kurath, U.S.P. 1800815; Moss and White, U.S.P. 1902255), ketones (*idem*, U.S.P. 1902256) and other groups. It forms an important condensation product with lignin (Phillips, U.S.P. 1750903). Some furfural resins are easily photosensitised and find application in lithography and etching of metals (Beebe, Murray and Herlinger, U.S.P. 1587269).

Furfural offers promise as a *fungicide, bactericide* and *herbicide*. Athlete's foot and swimmer's itch, both fungus diseases, yield to treatment with it, and it is also useful to destroy organisms that attack grain (Reddy, Phytopath. 1930, **20**, 147). An emulsion of kerosene (89), furfuraldehyde (10) and crude petroleum (1) is employed with success in the destruction of annual weeds especially dandelions (Melhus, U.S.P. 2007433). It is a preservative for glue and starch and for biological preparations. It has also been suggested for use as a fly repellant and in synthetic perfumes.

A recent patent claims that it is fatal to rats but harmless to all domestic animals except rabbits (de Wiczwinszky, F.P. 695394).

Mercury hydrofuramide has been used in the treatment of fungus diseases in wheat.

In its chemical properties furfural closely resembles benzaldehyde, giving *furoin* with KCN (Fischer, Annalen, 1882, **211**, 214) and a green dyestuff with dimethylaniline (Renshaw and Naylor, J. Amer. Chem. Soc. 1922, **44**, 862). It gives a *urethane*, m.p. 169°, and a *semicarbazone*, m.p. 202–203°. It is somewhat less sensitive to atmospheric oxidation than benzaldehyde, but more sensitive to light and acids.

Ammonia reacts in the cold with furfural to yield hydrofuramide, m.p. 117° $(C_4H_3O{\cdot}CH)_3N_2$ (Schiff, Ber. 1877, **10**, 1186). This compound is used as an accelerator and anti-oxidant in the manufacture of resins (Novotny and Kendall, U.S.P. 1705496).

Nitration of furfural with HNO_3 *d* 1·5 in acetic anhydride below −5° gives *5-nitrofurfural diacetate*, m.p. 92·5°, which on hydrolysis gives *5-nitrofurfural*, m.p. 75–76° (Gilman and Wright, J. Amer. Chem. Soc. 1930, **52**, 2550, 4165).

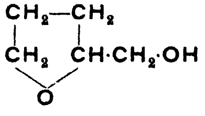
Furfural undergoes the Cannizzaro reaction with sodium hydroxide to give *furfuryl alcohol* $(C_4H_3O)CH_2{\cdot}OH$, b.p. 83°/24 mm., n_D^{21} 1·4869, and *furoic acid* (*pyromucic acid*),

$$(C_4H_3O)COOH,$$

m.p. 131–132° (Hurd, Garrett and Osborne, J. Amer. Chem. Soc. 1933, **55**, 1082). Furoic acid may also be obtained by the oxidation of furfural with permanganates, dichromates or catalytically. Esters of furoic acid have been suggested as plasticisers and solvents.

Under certain conditions furfuraldehyde may be oxidised to maleic acid, yields of 80% being claimed in one process (Zumstein, U.S.P. 1956482). This opens up the possibility of the commercial use of the Diels-Alder reaction.

Furfuryl alcohol is also prepared by the catalytic reduction of furfural using nickel (Padoa and Ponti, Atti. R. Accad. Lincei, 1906, **15**, II, 610), or iron (Pringsheim and Noth, Ber. 1920, **53** [B], 114). Using palladium black (Weinhaus, *ibid.* 1920, **53**, [B] 1656) or platinum black (Kaufmann and Adams, J. Amer. Chem. Soc. 1923, **45**, 3029; 1925, **47**, 1098) there are obtained furfuryl and tetrahydrofurfuryl



alcohol and various pentane diols. With unactivated PtO_2 the reaction stops at furfuryl alcohol (Pierce and Parks, *ibid.* 1929, **51**, 3384).

Furfuryl and tetrahydrofurfuryl alcohols are manufactured commercially using nickel catalysts (Peters, U.S.P. 1906873; I.C.I., B.P. 337296) and find application as solvents in the resin industry, for textile printing pastes

(Durand and Huguenin, F.P. 769171) and for paint removers (Mains, U.S.P. 1381485, 1483587) Furfuryl alcohol with HCl gives a jet-black resin used for the tops of laboratory tables (Fawkes, U.S.P. 1732124). Tetrahydrofurfuryl alcohol offers possibilities as a wetting agent (Bertsch, U.S.P. 1967656; H. Tr. Böhme A.-G., B.P. 393164, 402295) especially in the mercerisation of cotton (Soc. Chem. Ind. Basle, B.P. 431662).

Furfuryl xanthate has found commercial application as a flotation agent in ore refining (Keller, U.S.P. 1969269).

Furfuryl Ethers (Wissell and Tollens, Annalen, 1893, **272**, 303):

	b.p.	d_{20}^{20}
Methyl	134–136°	1·0315
Ethyl.	148–150°	0·9884
n-Propyl	164–166°	0·9722
Amyl	196–198°	—

Furfuryl Esters.—The ordinary methods of esterification cannot be employed as mineral acids resinify the alcohol. Resort must be had to the action of acid anhydrides or to Schollen-Baumann reactions. The following esters are water-white oily liquids with pleasant odours (Zanetti, Amer. Chem. J. 1925, **47**, 535):

	b.p. (corr.)		d^{20}
	760 mm.	1 mm.	
Acetate . . .	175–177°		1·1175
Propionate . . .	195–196°	59–60°	1·1085
Butyrate . . .	212–213°	69–70°	1·0530
Valerate . . .	228–229°	82–83°	1·0284
Benzoate . . .	*ca.* 275°	—	—

(Wissell and Tollens, *l.c.*).

FURIL, $C_{10}H_6O_4$, FUROIN, $OC_4H_3{\cdot}CO{\cdot}CO{\cdot}C_4H_3O$

Furfural behaves like an aromatic aldehyde undergoing the *acyloin* polymerisation in presence of potassium cyanide,

$$2OC_4H_3{\cdot}CHO{=}OC_4H_3{\cdot}CH(OH){\cdot}CO{\cdot}C_4H_3O$$

The acyloin (furoin) can be oxidised to the diketone (furil).

For the preparation of furoin, E. Fischer (Annalen, 1882, **211**, 218) boiled 40 parts of furfural, 30 parts of alcohol, 80 parts of water and 4 parts of potassium cyanide for 30–45 minutes and crystallised the product from a mixture of toluene and alcohol. Prisms, m.p. 135°. It gives a *methyl ether* (Irvine and McNicoll, J.C.S. 1908, **93**, 1610); *acetyl derivative*, m.p. 76–77° (Fischer) and two isomeric *oximes*, m.p. 160–161° and 102° respectively (A. Werner and Detscheff, Ber. 1905, **38**, 79; *see also* Macnair, Annalen, 1890, **258**, 222); *phenylhydrazone*, m.p. 79–81° (Macnair). Heat of combustion, 1097·7 kg. cal./mol. at const. vol. (Wrede, Z. physikal. Chem. 1910, **75**, 92).

For the oxidation of furoin to furil, E. Fischer (*l.c.* 221) dissolved 1 part of furoin in 12 parts of hot alcohol, rapidly cooled the solution and brought the fine crystalline separation into solution with a little caustic soda. An equal volume of water was added and air drawn through at 0° until the greenish-blue colour had given place to a dirty brown; precipitation was completed by the addition of water and the furil crystallised from alcohol. Yellow needles, m.p. 162°. Furil is obtained in 63% yield by oxidation of furoin (improved preparation given) with $CuSO_4$ in pyridine (Hartman and Dickey, J. Amer. Chem. Soc. 1933, **55**, 1228).

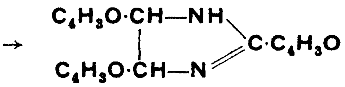
Furil gives α- and β-monoximes, m.p. 106° and 97–98° respectively, also α- and β-dioximes, m.p. 166–168° and 188–190° decomp. respectively (Macnair, *l.c.* 226). The α-dioxime (but not the β-compound) gives complexes with various metallic salts (Tschugaeff, Ber. 1908, **41**, 1681) and has been recommended for the estimation of nickel (*v.* Vol. II, 612*c*). The oxime, as obtained by refluxing furil with hydroxylamine hydrochloride in presence of methyl alcohol is sufficiently pure for the purpose, it is soluble to the extent of about 2% in boiling water and its nickel derivative has an approximate solubility of 1:6,000,000 in water and is less liable to contamination with unchanged dioxime than the corresponding benzildioxime salt (Soule, J. Amer. Chem. Soc. 1925, **47**, 982).

Furil yields a phenylhydrazone, m.p. 82–83°, and phenylosazone, m.p. 184° (Macnair, *l.c.* 225).

J. T. H.

FURINE, furfurine, 2:4:5-trifuryl-4:5-dihydroimidazole, $C_{15}H_{12}O_3N_2$, is prepared by converting furfuraldehyde into hydrofuramide with aqueous ammonia and effecting the cyclisation either with boiling dilute caustic potash (Bahrmann, J. pr. Chem. 1883, [ii], **27**, 313) or with liquid ammonia containing potassamide (H. H. Strain, J. Amer. Chem. Soc. 1930, **52**, 1216):

$$3C_4H_3O{\cdot}CHO{+}2NH_3$$
$$\rightarrow (C_4H_3O{\cdot}CH{:}N)_2CH{\cdot}C_4H_3O$$



Furine is a mono-acid base, m.p. 117°, soluble in organic solvents and in hot water, sparingly soluble in cold water; it forms an insoluble oxalate and a characteristic nitrate, m.p. 94° (Strain, *l.c.*), but melting at 182° after crystallising from alcohol-ether (Delépine, Bull. Soc. chim., 1888, [iii], **19**, 175, gives m.p. 154°). Furine yields *isofurine* on heating with sodium, and a *nitrosamine*, $C_{15}H_{11}O_4N_3$, in presence of nitrous acid (Schiff, Ber. 1878, **11**, 1250).

Furine has been proposed as a rubber vulcanisation accelerator (J. P. Trickey and G. J. Leuck, Ind. Eng. Chem. 1926, **18**, 812), furine is also claimed to have a beneficial effect on the ageing properties of vulcanised rubber (B.P. 315661), to be an inhibitor of the autoxidation of aldehydes (U.S.P. 1766760) and, adsorbed on infusorial earth, to act as a disinfectant and antiseptic (U.S.P. 1738740).

FUROIC ACID *v.* FURFURAL.

FUROIN *v.* FURIL.

FURUNCULIN. A medicinal preparation of dried yeast (Zellner and Wolff, Pharm.-Ztg. 1913, **58**, 1046).

FURYL ALCOHOL *v.* FURFURAL.

FUSANOLS. The names, α- and β-*fusanol*, were given by Sudborough and Rao (J. Indian Inst. Sci. 1922, **5**, 163) to two sesquiterpene alcohols which they claimed to have isolated from the wood oil of *Eucarya spicata*, the so-called West Australian sandalwood oil. The more recent investigations of Penfold (J. Proc.

Roy. Soc. N.S.W. 1928, **62**, 50; 1932, **66**, 240), however, have shown that these alcohols cannot have been homogeneous since the oil contains, in addition to the santalols, a primary alcohol having a very low density (*circa* 0·938), which is probably acyclic. There would appear to be no reason for retaining the names *α*- and *β*-fusanol in the literature.

J. L. S.

FUSEL OIL (Ger. Fuselöl; Fr. Huile de pommes de terre). This substance is produced in comparatively small quantities in the alcoholic fermentation of various bodies, *e.g.* potatoes, fruit, beetroot and grain. The proportion present varies according to the original substance, the condition of the mash and the method of fermentation. The alcohol obtained from potatoes usually contains the largest proportion. Alkaline liquids, particularly when warm and containing large quantities of sugar, promote its formation, while acid liquids, especially when containing tartaric, racemicor citric acids are said to prevent its production. The presence, in any quantity, of tartar or certain bitters such as that of hops also has an inhibitory effect, so that wines, etc., are usually free from fusel oil.

The proportion present in the alcohol finally produced also depends upon the method of rectification, that from pot stills containing higher proportions than the product of highly rectifying patent stills. When the latter are used, however, the amount of fusel oil obtained as a by-product naturally tends to increase. Thus the development of the commercial production of alcohol of very high strength has resulted in an increase in the quantity of fusel oil rejected during rectification. As an example, before 1923 no fusel oil was produced in the Philippine Islands. Now 1–5% of the crude alcohol produced is collected as fusel oil. Fusel oil is contained principally in those fractions of the alcoholic distillate boiling between 105° and 135°. Between 105° and 120° most of the *iso*-butyl alcohol is obtained whilst the amyl alcohols distil principally between 128° and 132°. According to Forte (Philippine J. Sci. 1924, **25**, 405), if a continuous still is used the fusel oil tends to collect at a point in the column where the alcoholic concentration is about 43% and it may be tapped off. If batch rectification is used the third and fourth fractions, containing 15–20% of fusel oil, are collected in a separating tank and rectifier. This has been confirmed by other workers although the distribution of the oil is affected by the conditions of rectification and it may easily be extended to higher fractions. Kilp and Deplanque (Z. Spiritusind. 1934, **57**, 306) have studied the formation of fusel oil in relation to the generation of alcohol in mashes made of potato flakes and molasses. They found that in the former alcohol was generated 1 hour before any fusel oil could be found whilst in the latter the fusel oil formation preceded that of the alcohol by 5 hours. Kilp (*ibid.* 219) also found that barley malt and oat malt mashes gave approximately the same fusel oil content. Higher alcohols are said to be rapidly produced after fermentation ceases. They, therefore, tend to increase the longer the interval between fermentation and distillation. This may be due to some organism other than yeast becoming active after the latter has ceased to work. Glimm and Stentzel (Z. ges. Brauw. 1931, **54**, 49, 57, 65) state that the production of fusel oil in beer depends on the time and temperature of storage, as well as on the amino-acid content of the wort, increasing to a maximum with increased time, after which it remains constant. The elimination of fusel oil from the final product has resulted in an increase in the proportion to be found in the spent wort, and Lühder (Z. Spiritusind. 1926, **49**, 286) points out the necessity for its removal if the residue is to be used as animal food.

Fusel Oil in Potable Spirits.—The injurious effect of raw or recently manufactured spirits has been attributed to the presence of fusel oil produced during the fermentation and not thoroughly separated. Bell considered it to be due rather to furfural and other empyreumatic bodies and this view was supported by Lauder Brunton, who thought that the toxic effect of spirit may also be attributed, in some cases, to the presence of traces of alkaloidal bodies, arising from the decomposition of albuminous substances in the mash. Schidrowitz also found in new whisky substances such as pyrrole, phenolic bodies, traces of nitriles, etc., which disappear as the spirit matures (J.S.C.I. 1905, **24**, 585). The actual adulteration of alcoholic liquors with fusel oil is improbable, but spirits containing 0·3% are usually deemed to be injurious, although the general tendency of the evidence given before the Royal Commission on Whisky and Potable Spirits was to show that the harmful effect of spirits is due to the ethyl alcohol itself rather than to fusel oil or other secondary products present. Prior to 1887 Beer recommended a maximum permissible limit of the fusel oil in brandy, liqueurs, etc., of 0·3%; but Bodländer and Traube (Rep. Anal. Chem. 1887, **7**, 167), who examined a number of commercial spirits, proposed a limit of 0·10–0·15%. Raw "brandy," produced in Switzerland from potatoes, maize and the residues from breweries, has been found to contain 1·32% of fusel oil. After filtration through charcoal it contained 0·2%, after rectification 0·06%, whilst after being subjected to both processes the product contained none (F. Pampe (Chem.-Ztg. 1887, **11**, 313). Kumamoto (J. Chem. Soc. Japan, 1932, **50**, 30) found the composition of sweet-potato fusel oil to be 90·8% alcohols, 0·9% acids, 2·4% esters, with a trace of organic bases and furfural. The alcohols consist of 77·4% *l*-amyl alcohol, 12·9% *iso*-amyl alcohol. In Scotch whisky containing 54·5% of alcohol, Dupré (Analyst, 1876, **1**, 6) found 0·19 parts of fusel oil in 100 parts by weight of alcohol, whilst Hamberg (Schmidts Jahrb. der Medicin, 1884, **201**, 27) found about 0·001% in beer. According to Bird (Int. Sugar J. 1927, **29**, 84) Demerara rum contained only a trace of fusel oil. Bird advanced this as an indication of the purity of the product.

Detection of Fusel Oil.—When a sample of spirit is poured on filter paper or on the hand and allowed to evaporate spontaneously, the characteristic odour of fusel oil may be recognised towards the close of the evaporation.

So small a proportion as $\frac{1}{2000}$ part of amyl alcohol in gin may thus be detected. On dissolving 1 g. of caustic potash in 150 ml. of the spirit, concentrating slowly to 15 ml. and adding an equal volume of dilute sulphuric acid, a powerful odour is given off which is frequently sufficiently distinctive to show the nature of the mash from which the spirit was obtained. Bettelli (Ber. 1875, **8**, 72) adds to the alcohol 6–7 vol. of water, and agitates with sufficient chloroform to produce a small layer after standing. This layer is drawn off and evaporated, and the residue tested by digestion with potassium acetate and sulphuric acid. In the presence of fusel oil the characteristic pear-like odour of amyl acetate is observable. Another method of detection is to dilute 40 ml. of the spirit with sufficient water to raise the density to about 0·980. The mixture is agitated with 15 ml. of chloroform, which after settlement is drawn off, shaken with an equal volume of water and evaporated. The residue is treated with a little water, a drop of sulphuric acid and sufficient of a strong solution of potassium permanganate to ensure that the liquid shall remain red after standing for 24 hours in a closed tube. The odour of valeric aldehyde is frequently noticeable shortly after the addition of the permanganate, but the characteristic smell of valeric acid, on which this very delicate test is based, is not appreciable until after standing.

Estimation.—The accurate estimation of fusel oil in spirit is extremely difficult. A very rapid and simple process introduced by Traube is said to give satisfactory results where great accuracy is not required. The specific gravity of the spirit having been determined, sufficient water is added to reduce the proportion of alcohol to 20%. The liquor is sucked up and allowed to fall a few times in a carefully dried, thin-sided capillary tube, 20 cm. long and about 0·8 mm. in diameter, fastened to a graduated scale, this terminates at the zero in two points which are set to the surface of the liquid by the adjusting screws on the stand which holds the apparatus in the vessel into which the capillary tube dips. The height to which the liquid rises decreases with a rise in the proportion of fusel oil. From the observed height of the liquid in the capillary tube (temperature 21°), the percentage of fusel oil may be ascertained from the following table:

Height in tube in mm.	Percentage of fusel oil	Height in tube in mm.	Percentage of fusel oil.
53·6	0·0	48·85	0·6
52·7	0·1	48·20	0·7
51·85	0·2	47·45	0·8
51·0	0·3	46·75	0·9
50·3	0·4	46·15	1·0
49·6	0·5		

This process is said to be largely affected by accidental conditions, such as temperature or moisture in the tube and by the presence of nitrobenzene and various flavouring oils. Further information on this process is given by Traube (Bied. Zentr. 1900, **15**, 559; Ber. 1886, **19**, 892; Chem. News, 1886, **53**, 302; Rep. Anal. Chem. 1886, **6**, 659), Stutzer and Reitmair (*ibid.* 1886, **6**, 606), and Girard and Cuniasse ("L'Analyse des Alcools," Masson Paris, 1899,). An improved apparatus, which he calls a "stalagmometer" was introduced by Traube (Ber. 1887, **20**, 2644) for this estimation. The liquid, diluted as above to 20%, is filled to a mark in a vessel and is allowed to fall drop by drop through a capillary tube at the base of the vessel, the number of drops being noted as compared with the number of drops of pure alcohol of the same strength falling from the same apparatus. A smaller proportion of fusel oil than 0·05% may thus be determined. The following table by Girard and Cuniasse (*op. cit.*) serves to indicate the percentage of fusel oil corresponding with the number of drops observed:

Number of drops.	Percentage of fusel oil.	Number of drops.	Percentage of fusel oil.
100	0·0	108·5	0·6
101·8	0·1	109·9	0·7
103·6	0·2	111·5	0·8
105·0	0·3	113·1	0·9
106·3	0·4	114·7	1·0
107·5	0·5		

If the temperature of the spirit is higher or lower than that for which the instrument has been calibrated, the number of drops observed is increased or diminished by 0·1 drop for every 30 drops for each degree of difference.

Another process depends upon the alteration produced by the presence of fusel oils in the volume of the chloroform extract of 100 ml. of alcohol and is officially recognised in Germany and Switzerland. A modification of the apparatus consists of a pear-shaped bulb holding about 200 ml., stoppered at the upper end, and having at the lower end a graduated stem of about 4 mm. internal diameter leading to another bulb of about 20 ml. capacity and terminating in a tube provided with a stop-cock. The narrow stem is graduated in 0·02 ml. from 20·0 to 22·5 ml. Fusel-free alcohol is first prepared by fractional distillation over caustic alkali to resinify aldehydes, saponify esters, and saturate acids, and is diluted with water to a sp.gr. of 0·965 at 15·6°. A quantity of chloroform is dehydrated and redistilled, and a solution of sulphuric acid of sp.gr. 1·2857 at 15·6° is prepared. Of the sample under examination 200 ml. is taken, made alkaline, and about 175 ml. distilled over. Twenty-five ml. of water is added to the distilling flask and the distillation continued to 200 ml. The distillate is diluted with water to a sp.gr. of 0·965 at 15·6°, and this with the Röse apparatus and the flasks containing the reagents (fusel-free alcohol, chloroform and sulphuric acid) are placed in a water bath kept exactly at 15° until all have acquired a uniform temperature. The apparatus is then filled by suction through the lower tube to the 20 ml. mark with chloroform and 100 ml. of fusel-free alcohol and 1 ml. of sulphuric acid added through a pipette. The apparatus is inverted and shaken vigorously for 2 or 3 minutes, the stop-cock being momentarily opened once or twice to equalise pressure. The apparatus is then allowed to stand for 10 or 15 minutes in the water bath at 15°, with occasional turning to hasten the separation of the reagents, and the volume of the chloroform is noted. The apparatus is then thoroughly cleaned and dried and the operation repeated, using the distillate from the sample instead of the fusel-free alcohol. An increase in the volume of the chloroform is observed due to the fusel oil present, and this difference, multiplied by the factor 0·663, gives the volume of fusel oil in 100 ml., or the percentage of fusel oil by volume in the 30% distillate. This is then calculated to the percentage of fusel oil by volume in the original sample according to the alcoholic strength of the latter. Kilp and Lampe (Z. angew. Chem. 1928, **41**, 1163) using the Röse "shaking burette" applied the formula $Z\ 0{\cdot}5428V/a=g.$ fusel oil in 100 c.c. original liquid in which Z=volume increase of chloroform, V=total volume of solution, and a=aliquot part of original solution. The value 0·5428 represents the grams of amyl alcohol corresponding to the increase of 1 ml. in volume of the chloroform. A. Frey (Z. Spiritusind. 1934, **57**, 190) states that accurate results can be obtained by this method only if the chloroform used is of the highest purity, any impurities present tending to give a low result.

In France the official method is that of Savalle as modified by Girard and Cuniasse (*op. cit.*) and is based upon the depth of colour obtained by the action of strong sulphuric acid upon the higher alcohols. The method gives only comparative results and requires the observance of conditions so strict as to be almost unattainable in normal practice. Another method, devised by Beckmann (Z. Nahr.-Genussm. 1901, **4**, 1059) depends upon the separation of the higher alcohols from the spirit by means of calcium chloride and carbon tetrachloride, the conversion of the higher alcohols into their nitrites by the action of sodium nitrite and sodium bisulphate, removing the excess of nitrous acid with sodium bicarbonate, decomposing the nitrites with sulphuric acid and final titration of the nitrous acid, thus obtained, with permanganate. Schidrowitz (Analyst, 1905 and 1906) considers this method unreliable, however, owing chiefly to the extraction of ethyl alcohol by the carbon tetrachloride.

Budagjan and Ivanova (Z. Unters. Lebensm. 1932, **63**, 200) have suggested a modification of Komarowski's method, in which the distillate adjusted to 50% by volume of ethyl alcohol is treated with dilute sulphuric acid, potash, and silver nitrate and redistilled, the acetaldehyde content being determined by Mohler's method. Another portion of the second distillate is treated with salicylaldehyde and dilute sulphuric acid, the colour being matched against standards containing amyl alcohol and the MeCHO found.

Possibly the best method hitherto suggested is that of Marquardt (Ber. 1882, **15**, 1661) as modified first by Allen (Analyst ,1891, **16**, 102) and later by Schidrowitz (J.S.C.I. 1902, **21**, 814). It is based upon the oxidation of the higher alcohols into the corresponding acids, and the estimation of the latter by titration or by converting them into and weighing their barium salts. The extraction is carried out as in the Beckmann process. To the washed carbon tetrachloride solution 5 g. of pure powdered potassium dichromate, 2 ml. of concentrated sulphuric acid and 10 ml. of water are added. The mixture is shaken and gently boiled for 8 hours under a reflux condenser. It is cooled, a little pumice and 50 ml. of recently boiled distilled water added, and it is then distilled to near dryness. The residue is cooled, 50 ml. of water added and again distilled. The distillates are mixed and titrated with $N/10$ baryta solution, first with Methyl Orange as indicator, and then with phenolphthalein. The acid indicated by the Methyl Orange is regarded as "mineral acid" and the difference as organic acid, which is calculated into amyl alcohol by multiplying the number of ml. of baryta solution by 0·0088 and the figure indicating the dilution of the alcohol. To obtain the combining weight, the solution containing the barium salt of the acid is separated from the carbon tetrachloride, evaporated, filtered and finally dried in a platinum capsule and weighed. The weighed residue is then treated with a slight excess of sulphuric acid, again evaporated, and the barium sulphate ignited and weighed. From the weights found the combining weight of the acid is calculated. By this method also some ethyl alcohol is extracted by the carbon tetrachloride, but it is suggested that this does not appear as acetic acid after oxidation. According to Schidrowitz the effect attributed to "mineral acid" (of the presence of which there is no proof) may be due to some action between the Methyl Orange and certain aliphatic acids present. Penniman and others (Ind. Eng. Chem. [Anal.], 1937, **9**, 91) have advanced various criticisms of this method and certain modifications which they claim afford a very speedy and accurate determination.

Composition.—Whilst the proportion of fusel oil produced depends upon the source of production, the nature of the ferments and the method of distillation, the composition of the oil is also affected by these conditions. As a generalisation it may be stated that fusel oil consists mainly of two alcohols one of which, *iso*butyl carbinol or *iso*amyl alcohol or inactive amyl alcohol, is optically inactive whilst the other, *sec*-butyl carbinol or active amyl alcohol, rotates the plane of polarised light to the left sufficiently to render the product strongly lævorotatory. The following alcohols are said to have been separated from fusel oil:

Ethyl, $CH_3{\cdot}CH_2{\cdot}OH$.
n-Propyl, $C_2H_5{\cdot}CH_2{\cdot}OH$.
*iso*Propyl, $(CH_3)_2{\cdot}CH{\cdot}OH$.
n-Butyl, $C_3H_7{\cdot}CH_2{\cdot}OH$.
*iso*Butyl, $(CH_3)_2CH{\cdot}CH_2{\cdot}OH$.
tert-Butyl, $(CH_3)_3C{\cdot}OH$.
Active amyl, $C_2H_5(CH_3)CH{\cdot}CH_2{\cdot}OH$.
Inactive amyl, $(CH_3)_2C,H{\cdot}CH_2{\cdot}CH_2{\cdot}OH$.
Methyl *n*-propyl carbinol, $CH_3(C_3H_7)CH{\cdot}OH$.
Normal primary amyl alcohol, $C_5H_{11}{\cdot}OH$.
A primary hexyl alcohol, $C_6H_{13}{\cdot}OH$.
A primary heptyl alcohol, $C_7H_{15}{\cdot}OH$.

Of the acids present: formic, acetic, propionic, butyric, valeric, caproic, œnanthic, caprylic, pelargonic and capric have been identified whilst the presence of ethyl acetate and other esters and various aldehydes has also been established.

The fusel oil from grain or potatoes consists largely of amyl alcohols with ethyl alcohol the inactive amyl alcohol being the principal constituent. According to Rabuteau (Compt. rend. 1879, **87**, 500) the following represents the approximate percentage volume composition of *potato oil*:

*iso*Propyl alcohol	15·0
n-Propyl alcohol	3·0
n-Butyl alcohol	6·5
*iso*Butyl alcohol	5·0
Inactive amyl alcohol	27·5
Active amyl alcohol	6·0
Products boiling above 132° and retaining amyl alcohol . . .	17·0
Ethyl alcohol, ethyl acetate and aldehyde	7·5
Water	12·5

Later observations, however, do not confirm Rabuteau's statement as to the presence of *iso*propyl alcohol. Ordonneau (Compt. rend. 1886, **102**, 217) found in commercial alcohols from maize, beet and potatoes, in addition to other substances, propyl alcohol, active and inactive amyl alcohol, pyridine, a base which he considered to be collidine, and *iso*butyl alcohol. He did not find a trace of *n*-butyl alcohol. Karl Windisch ("Arbeiten aus dem kaiserlichen Gesundheitsamt," 1892, Bd. 8) gives the following respective compositions of potato and corn fusel oil, expressed in grams per kilogram and excluding ethyl alcohol and water:

	Potato.	Corn.
n-Propyl alcohol . . .	68·54	36·90
*iso*Butyl alcohol . . .	243·50	157·60
Amyl alcohol	687·60	758·50
Hexyl alcohol	—	1·33
Heptyl alcohol	—	trace
Free fatty acids . . .	0·11	1·60
Fatty acid esters . . .	0·20	3·05
Furfurol and bases . . .	0·05	0·21
Terpenes	—	0·33
Terpene hydrate . . .	—	0·48

He also analysed the free fatty acids and acid esters with the results given in the table at the top of the next column expressed in percentages, the acids and esters being taken together in the potato fusel oil and separately in the fusel oil from corn.

Yoshitomi *et al.* (J. Pharm. Soc. Japan, 1922, **486**, 661) found that the fusel oil obtained from Japanese sweet-potato brandy had d^{14} 0·8382, acid number 2·828, saponification number 36·7 and an ester value of 33·8. They found that 1 lb. of fusel oil contained 31·8 g. of fatty acids (of which nearly 25 g. was palmitic) which, when crystallised from alcohol, were free from the characteristic fusel-oil odour and could be used in the manufacture of soap.

	Potato.	Corn.	
	Free fatty acids and esters.	Free fatty acids.	Esters.
Capric . . .	36	44·1	40·7
Pelargonic . .	12	12·9	14·2
Caprylic . . .	32	26·7	34·8
Caproic . . .	14	13·2	9·6
Butyric . . .	0·5	0·4	0·4
Acetic	3·5	2·7	0·3

According to Stevenson (Texas State J. Med. 1925, **20**, 562) the fusel oil from corn whiskey contained, per 1,000 parts, 750 parts of *iso*propyl alcohol, 180 *n*-propyl alcohol, 40 *iso*butyl alcohol and 20 amyl alcohol. Schorigin and co-workers (Ber. 1933, **66** [B], 1087) have examined the high boiling fractions of fusel oil obtained chiefly from potato spirit. They found 36% of alcohols, 13% saturated aliphatic acids, and 4·5% organic bases. They isolated in pure form the ethyl esters of caproic, caprylic, capric, lauric, myristic and palmitic acids; hexyl, heptyl, octyl and nonyl alcohols; and trimethyl-, tetramethyl-, diethyl- and triethylmethylpyrazine.

The fusel oil prepared in the South of France from the marc of brandy contains *n*-propyl alcohol in considerable quantities. Ordonneau (*l.c.*) recommends that the fermentation of a mash should be performed with the elliptic *wine* yeast instead of the globular *beer* yeast, as he finds by experiment that the former produces the *n*-butyl alcohol, while the latter tends to form the *iso*-variety. He attributes the disagreeable smell of the oil from the ordinary mash to the *iso*butyl alcohol present, the more agreeably smelling wine brandy containing *n*-butyl and no *iso*butyl alcohol. Other workers also suggest that the ferment in brewer's yeast (*Saccharomyces cerevisiæ*) appears to favour the production of *iso*butyl alcohol whilst *Saccharomyces ellipsoidens* from the grape tends to produce *n*-butyl alcohol. By fractionation of wine brandy 25 years old Ordonneau (*l.c.*) obtained the following:

	Per cent. by volume.
Aldehyde	0·003
Ethyl acetate	0·035
Acetal	traces
Œnanthylic ester	0·004
Propionic, butyric and caproic esters	0·003
n-Propyl alcohol.	0·040
n-Butyl alcohol	0·218
"Amyl alcohol"	0·0838
Hexyl alcohol	0·0006
Heptyl alcohol	0·0015
Amine bases (probably of the pyridine series)	traces

According to Le Bel (Compt. rend. 1883, **96**, 1368) natural white wine contains 0·2% of amyl alcohol. Swenarton (Science, 1929, **70**, 554) found that crude fusel oil from molasses-fermentation contains, in addition to *n*-propyl and *iso*butyl alcohol, *sec*butyl carbinol, and *iso*butyl carbinol, alcohols of the hexyl, heptyl, octyl, nonyl and decyl series and other bodies.

Removal of Fusel Oil from Spirits.—Apart from the desirability of removing the fusel oil from spirits intended for human consumption, the oil recovered as a by-product is valuable for certain commercial purposes. As already stated, the fusel oil can be rapidly and almost completely removed during the process of rectification of the alcohol in the modern patent still. When, however, the alcohol as commercially produced, *e.g.* pot-still spirit, contains an appreciable proportion of fusel oil other methods must be adopted for its removal. These usually involve the addition to the alcohol of some substance which will absorb the fusel oil and can then be separated from the defuselised alcohol. In some cases the fusel oil is lost whilst in others it can be recovered and is available for commercial use. Among the various substances proposed are charcoal, soap, oil, potash, pearl ash, lime, sulphuric, nitric and hydrochloric acids, bleaching powder and potassium permanganate. Charcoal, soap and oil are supposed to separate the fusel oil unchanged. When rectified over potassium permanganate or bleaching powder the amyl alcohols are converted into valerates, but a portion of the ethyl alcohol is also decomposed. When bleaching powder is used the mass is allowed to digest for some time, after which the spirit is drawn off and rectified. It has been suggested that, if the spirit be distilled from hard soda soap, the fusel oil remains with the soap from which it may be separated by subsequent distillation at a higher temperature.

The most approved method of separation is by well-burnt granulated vegetable charcoal or bone-black. The charcoal is placed upon perforated trays in a vessel surrounded by a cooling jacket and the spirit, suitably diluted, is caused to pass through several such trays. The operation should not be performed above the ordinary temperature, as the fusel oil is again dissolved from the charcoal near the boiling temperature. From 3 to 5 vol. of charcoal are required for the successful treatment of 100 vol. of brandy. The fusel oil is evolved from the charcoal on treatment with superheated steam and the charcoal may be repeatedly used after heating to redness to drive off any occluded substances.

In the preparation of alcohol as motor fuel the elimination of fusel oil is desirable, and this is usually accomplished by treatment with active carbon as above. A. E. Williams (Chem. Trade J. 1934, **95**, 111) points out that oxidation due to the air contained in the interstices of the carbon may be avoided by agitating the carbon under vacuum at a temperature of 30° or less and the ethyl alcohol is removed by passing an inert gas through the carbon. Williams states that a good vegetable carbon will adsorb eight times its weight of fusel oil.

Synthetic Fusel Oil.—Various methods have been advanced for the commercial preparation of substitutes for fusel oil. In that described by Essex, Hibbert and Brooks (J. Amer. Chem. Soc. 1916, **38**, 1368) a gasoline boiling at 25–45° and consisting chiefly of saturated hydrocarbons is chlorinated by introducing chlorine at one end of a mass of the hydrocarbon whilst illuminating the other end with a source of actinic light and causing the gas to approach the light. By this means monochloro-derivatives are obtained and, as soon as these have accumulated to the extent of 20%, the mixture is fractionated and the unchanged hydrocarbons are recovered for retreatment. The fraction, b.p. 95–140°, consisting mainly of pentyl and hexyl chlorides, is heated with an equal weight of anhydrous sodium acetate (with or without acetic and amyl acetate) for 5 hours at 200° under pressure in an autoclave rotated 30 times per minute. In this way 580 lb. of the crude chlorides gave 384 lb. of crude amyl acetate from which fusel oil may be obtained by hydrolysis. In another method suggested by two of these investigators—Brooks and Essex (U.S.P. 1221667, 1917)—the chlorides are heated with methyl alcohol and a formate under pressure at 140–190°.

Commercial Uses.—Fusel oil is largely used for the manufacture of amyl acetate which has numerous applications in the arts and manufactures, in flavouring essences (pear oil, etc.) for confectionery, as a solvent for celluloid and in making lacquers, varnishes, artificial leather, waterproofing and sanitary sheeting for hospitals. It is also used in toxicology as a solvent for alkaloids, for which purpose it should be carefully purified by agitation with dilute acid to remove an alkaloidal body which it is liable to contain. On account of its strong affinity for chlorine, fusel oil has been employed in chlorine generators for laboratory purposes as an absorbent for that gas, to prevent its escape into the atmosphere when the supply is no longer required, whilst its principal constituent (amyl alcohol) is employed in the estimation of fat in milk by the centrifugal method (B.S. No. 696, Pt. 2, 1936). The *iso*amyl alcohol (inactive amyl alcohol) may be separated from fusel oil by agitation with a saturated solution of common salt. The amyl, butyl and propyl alcohols, which are less soluble in that medium than in water, separate as an oily layer, while the ethyl alcohol remains in the brine. The separated oil is distilled, the portion coming off between 105° and 120° consisting principally of *iso*butyl alcohol, while that distilling between 125° and 140° contains the amyl alcohols. This is collected separately, agitated with hot milk of lime, dried over calcium chloride and redistilled, the portion coming off between 128° and 132° being collected separately. In this way the *iso*amyl alcohol is obtained almost free from butyl alcohol and from valeric aldehyde. The barium amyl sulphate produced from active amyl alcohol is 2½ times as soluble in water as that from the inactive variety, so that these salts may be separated by fractional crystallisation and afterwards treated for regeneration of the alcohols.

The amyl alcohols of fusel oil dissolve in about 40 parts of cold water. According to Balbiano (Ber. 1876, **9**, 1437) the inactive variety is soluble in about 50 parts of water at 14° and is less soluble at 50°. *iso*Butyl alcohol dissolves in 10 parts of water at 15°. One part of inactive amyl alcohol takes up about 0·08 parts of water, while *iso*butyl alcohol dissolves nearly twice that amount. By a contact dehydration process Konek (Matematik Fermészettudományi Ertisito, 1925, **41**, 9) has produced a mixture of isomeric amylenes from fusel oil. A mixture of these hydrocarbons with double the volume of benzene and of ethyl alcohol gave a satisfactory motor fuel. Kino (J. Soc. Chem. Ind. Japan, 1928, **31**, 749) found that when the fusel oil obtained from *kaoliang* was treated with **KOH**, potassium palmitate crystallised out in a nearly pure state. In order to obtain suitable solvents for the preparation of lacquers Hsien Wu Ting (Chiao Tung Univ. Research Inst. Ann Rpt. Bur. Chem. 1936, **3**, 75) esterifies the fusel oil and fractionates the esters, the various fractions being evaluated according to their solvent power on nitrocellulose.

Estimation of Ethyl Alcohol in Fusel Oil.—Fusel oil containing not more than 15% of proof spirit is allowed to be delivered from distilleries in the United Kingdom and also to be admitted duty free on importation from abroad. The determination of the ethyl alcohol is therefore of considerable importance, but although various methods have been suggested none can be accepted as free from objection. The method commonly adopted in this country as sufficiently accurate for all practical purposes is as follows: 75 ml. of the sample is shaken vigorously for 4 or 5 minutes in a separator (A) with 150 ml. of water and allowed to stand. If an emulsion forms a few grains of salt are added. The aqueous layer is drawn off into a second separator (B), saturated with salt, and extracted with 150 ml. of petroleum ether. The brine layer is then drawn off into a third separator (C) and extracted with a further 150 ml. of petroleum ether and the brine run off into a distilling flask. The oil remaining in (A) is treated a second time with 150 ml. of water, the aqueous layer drawn off into the petroleum ether in (B), saturated with salt and extracted. The brine layer is drawn off into (C) and there extracted with the petroleum ether, from which, after separation, it is run into the distilling flask. The treatment of the oil remaining in (A) is repeated throughout. The 450 ml. of brine is distilled and the first 75 ml. of the distillate collected. This portion is saturated with salt and extracted with 150 ml. of petroleum ether. The brine is run off, distilled, 75 ml. collected and the specific gravity and Zeiss immersion-refractometer reading of this fraction determined. The refractometer reading will be somewhat higher than that of ethyl alcohol of the same density. The difference is multiplied by the appropriate factor (1·1 is taken in ordinary cases) and the product is deducted from the percentage of proof spirit as deduced from the specific gravity of the distillate. Macoun (Analyst, 1933, **58**, 664) prefers a method in which to 20 ml. of the oil in a 50 ml. Eggertz tube (graduated to 0·1 ml.) 5 g. of K_2CO_3 is added. This is well mixed. More carbonate is added if the original all dissolves or water is added if there is no line of demarcation between the two liquid phases. The volume of the upper layer is noted. Another 20 ml. of the sample is placed in a "tar acid flask" of 225 ml. capacity which is graduated from 0 to 25 ml. in not more than 0·2 ml. intervals. A saturated solution of fusel oil in saturated **NaCl** solution is added until the flask is about ¾ full. From 4 to 5 ml. of concentrated hydrochloric acid and exactly 5 ml. of petroleum ether are added. The whole is well shaken and sufficient salt solution added to make the total volume 225 ml. After further shaking and standing until the layers have separated out, the volume of the upper layer is noted. Let A represent the contraction from 20 ml. observed in the Eggertz tube and B the contraction from 25 ml. observed in the flask. The percentage of ethyl alcohol is (B–A) × 0·93 × 5.

Water Content of Fusel Oil.—Bakowski and Treszczanowicz (Przemysł Chem. 1937, **21**, 204) suggested an azeotropic method for the determination of water in fusel oil. In a special apparatus designed to give an easy and accurate reading of the volume of water collected they use methylene chloride which forms with water an azeotropic mixture boiling at 38·45°.

F. G. H. T.

FUSIBLE METALS (*v.* Vol. I, 698*b*).

FUZE POWDER (*v.* Vol. IV, 459*b*).

G

GABBRO. A holocrystalline igneous rock composed essentially of basic plagioclase-felspar and augite, and containing less than about 50% of silica. It is the plutonic equivalent of the finer-grained dolerite and basalt, having crystallised slowly under considerable pressure from large bodies of molten material within the earth's crust. The felspar is the soda-lime labradorite or the lime-felspar anorthite; the augite is usually the laminated diallage variety; apatite, iron-ores (magnetite and ilmenite) are usually present in small amount. When the orthorhombic pyroxene hypersthene is present in addition to plagioclase and augite the rock is called a *norite*. The more acid quartz-gabbro forms a passage to diorite, whilst the more basic olivine-gabbro grades into the peridotites The rock is dark grey, black, or greenish-black in colour, medium to coarse grained in texture, and very hard. Sp.gr. 2·7–3·0 (weight per cu. ft. 170–190 lb.); crushing strength 640–2,200, average 1,830, tons per sq. ft.

Analysis I of olivine-gabbro from Skye; also Cr_2O_3 trace (W. Pollard, 1900). II, olivine-gabbro from Lizard, Cornwall; also Cr_2O_3 0·08, V_2O_3 0·02, Li_2O trace, FeS_2 0·11 (E. G. Radley, 1912). III, Quartz-gabbro from Carrock Fell, Cumberland (G. Barrow, 1894). IV, Kentallenite from Kentallen, Argyllshire; also Cr_2O_3 0·10, (Co,Ni)O 0·07, CO_2 0 16, Cl trace (W. Pollard, 1900).

Gabbro forms large masses and is of wide

	I.	II.	III.	IV.
SiO_2	46·39	50·69	53·50	52·09
TiO_2	0·26	0·42	0·45	0·73
Al_2O_3	26·34	20·56	22·20	11·93
Fe_2O_3	2·02	1·55	3·60	1·84
FeO	3·15	3·10	2·64	7·11
MnO	0·14	0·16	0·35	0·15
MgO	4·82	6·84	2·00	12·48
CaO	15·29	11·99	9·45	7·84
Na_2O	1·63	3·36	4·26	0·24
K_2O	0·20	nil	0·61	3·01
P_2O_5	0·58	0·05	—	0·34
H_2O	trace	1·12	1·50	0·35
	100·82	100·84	100·56	98·11
Sp.gr.	2·85	—	2·80	2·94

distribution, occurring, for example, in the Highlands of Scotland, Lendalfoot in Ayrshire, Carrock Fell in Cumberland, North and South Wales, the Lizard district in Cornwall, and in Guernsey. Owing to its dull colour and difficulty of working, it is not very extensively employed as a building stone; and it is reputed not to weather well, especially those varieties containing more felspar. In the trade it often passes under the name of "black granite" (on the other hand, the trade name "Norwegian gabbro" is sometimes applied to the augite-syenite—*laurvikite*—from the south of Norway). Medium-grained varieties are used for road metal and paving-sets. Olivine-gabbro is extensively quarried for export at Herrestad near Kärda in province Jönköping, Sweden, and on the Pleasant river near Addison in Maine, U.S.A. The "black granite" of the Kentallen quarries in Argyllshire is a dark bluish-grey, medium-grained alkali-gabbro containing orthoclase, olivine and biotite in addition to the usual constituents, and has been named *kentallenite*. It is used principally for paving-sets, and on a polished surface it displays bright plates of mica.

Gabbro takes a good polish and is sometimes used for ornamental purposes. The diallage often displays a metallic sheen, and in the gabbro of Volhynia and near Kiev in Russia the labradorite sometimes shows blue reflections. Coarse-grained gabbros when partly altered show the light- and dark-coloured minerals in marked contrast, and have been used as far back as Roman times as ornamental stones. In some cases the felspar is altered to saussurite and the diallage to emerald-green smaragdite, the rock being then known as *euphotide*; this beautiful ornamental stone occurs in the Alps, Corsica ("Verde di Corsica"), and Elba. A dark-coloured orbicular gabbro from Dehesa, San Diego Co., California, has also been used as an ornamental stone.

Magmatic segregations of iron-ores, metallic sulphides (nickeliferous pyrrhotine and chalcopyrite) and apatite sometimes occur in connection with gabbro masses.

L. J. S.

GADOLINITE. A rare mineral consisting of silicate of yttrium earths, beryllia and ferrous oxide, $Be_2FeY_2Si_2O_{10}$. Analyses show about 40–45% of yttrium earths of molecular weight 250–290; the amount of erbia has been separately determined as 10–15%. It occurs in much larger masses than the other rare-earth minerals, forming rough, black and opaque crystals up to 500 kilos. in weight. The crystals are monoclinic with an orthorhombic aspect; but in thin sections the material is optically isotropic. When heated, the mineral suddenly glows brightly, a molecular transformation taking place; the material then becomes optically birefringent, increases in sp.gr. (from 4·1–4·4 to 4·4–4·7), and changes in colour (as seen in sections) from greenish to reddish. Gadolinite occurs in some abundance as masses of considerable size in pegmatite veins at a few localities; notably, at Ytterby and near Fahlun in Sweden; in the felspar quarries of Setersdal and Hitterö, and elsewhere in the south-east of Norway; Llano Co. in Texas, Mohave Co. in Arizona, Western Australia and Japan. The locality (Barringer Hill, 5 miles south of Bluffton) in Llano Co. has yielded masses of gadolinite weighing 200 lb., in association with several other rare-earth minerals. These have been worked for the supply of yttrium and erbium earths used in the "glower" of the Nernst lamp (W. E. Hidden, Amer. J. Sci. 1889, **38**, 474; 1905, **19**, 425).

L. J. S.

GADOLEIC ACID (*v.* Vol. III, 247*b*).

*iso***GADOLEIC ACID** (*v.* Vol. II, 522*d*).

GADOLINITE (*v.* Vol. II, 512*b*; IV, 245*c*, 321*c*).

GADOLINIUM, Gd. Atomic number 64; atomic weight 156·85±0·001 (Naeser and Hopkins, J. Amer. Chem. Soc. 1935, **57**, 2183); 156·9±0·2 (Aston, Proc. Roy. Soc. 1934, A, **146**, 54); isotopes 155, 156, 157, 158, 160 (Aston, *l.c.*).

This element was first identified by Marignac in 1880, who separated its salts from those of other rare-earth metals present in samarskite by fractional precipitation with potassium sulphate (Arch. de Genève, 1880, [iii], **3**, 413; Compt. rend. 1880, **90**, 899). With europium and terbium, gadolinium forms the small group of terbium metals, and as the solubilities of its salts are intermediate between those of the other two members of the family, the final separation of gadolinium from these elements is a matter of considerable difficulty. The older methods of separation, precipitation by ammonia, crystallisation of the oxalates, formates and double sulphates, or combinations of these processes, did not, in all probability, lead to the complete purification of the element (Meyer and Müller, Z. anorg. Chem. 1919, **109**, 1). The presence of small quantities of terbium is indicated by a faint yellow discoloration of the colourless gadolinia. Europium is detected spectroscopically in the arc spectrum.

Sources and Extraction.—Samarskite, gadolinite, ytterbite, xenotime, fergusonite, the crude yttrium earths from monazite, etc.

Some of these may be decomposed by HCl or H_2SO_4 while others must be fused with sodium pyrosulphate. Hydrofluoric acid is often a useful reagent for attacking some of the minerals as the insoluble rare-earth fluorides may then be easily separated from fluorides of such metals as niobium, tantalum, tungsten and zirconium which are soluble in the diluted acid. These and other metals, the chlorides of which are readily volatile, may also be removed by heating the mineral in a stream of sulphur chloride or phosgene.

After separating the heavy metals, thorium and cerium (if present in appreciable amount), the rare-earth metals are usually precipitated as the oxalates, ignited to the oxides and these converted into suitable salts which are fractionated so as to divide the rare earths into groups. The precise methods to be adopted in any particular case will depend largely upon the composition of the mixed earths, but the following are typical of those commonly employed.

(1) *Fractional Precipitation of the Sodium or Potassium Sulphates.*—If an aqueous solution of a mixture of rare-earth chlorides or nitrates is treated with a saturated solution of the alkali sulphate the double sulphates are precipitated. When this process is carried out fractionally the cerium group separates first while the yttrium earths collect in the mother liquor. The salts of the terbium fraction are intermediate in solubility and divide themselves between these groups, it being usually arranged that gadolinium shall be precipitated with the cerium earths particularly when the amount of the latter is small. Further separation is then effected by fractionation of the bromates or the rare-earth magnesium nitrates. When the concentration of the cerium group is considerable it is better to commence with the double magnesium nitrate separation (Marignac, *l.c.*; Delafontaine, Ann. Chim. Phys. 1878, [v], **14**, 238; James, J. Amer. Chem. Soc. 1908, **30**, 182; 1911, **33**, 1326; 1912, **34**, 757; Meyer and Müller, *l.c.*; *cf. also* de Boisbaudran, Compt. rend. 1883, **97**, 1463).

(2) *Fractional Crystallisation of the Nitrates.*—Although gadolinium nitrate is the least soluble of the rare-earth nitrates in nitric acid, the differences in solubility are comparatively small so that quicker separation is achieved by employing certain double nitrates. Of these the rare-earth magnesium nitrates are the most commonly used in the preliminary separations, and fractionation of their aqueous solutions causes lanthanum, praseodymium and neodymium quickly to collect in the head fractions and to be separated from samarium, europium, gadolinium, terbium and the yttrium metals. After their removal crystallisation is continued from nitric acid (30%) instead of water and samarium is now separated from the least soluble fractions. Bismuth magnesium nitrate is then added and fractionation continued until intermediate fractions of pure bismuth double salt are obtained. As the solubility of this salt lies between those of europium and gadolinium magnesium nitrates it follows that the head fractions will contain the less soluble europium free from gadolinium while the tail fractions will consist of gadolinium, terbium, etc., together with excess of the bismuth double nitrate. Bismuth is now removed from these fractions and the rare earths are converted, through the oxalates and oxides, into the simple nitrates which are crystallised so as to collect gadolinium and terbium in the least soluble fractions. These are then separated from each other by continuing the fractionation in the presence of bismuth nitrate which has a solubility intermediate between that of gadolinium and terbium nitrate. Separation of these two may also be achieved through the double nickel nitrates or dimethyl phosphates or by fractional precipitation with ammonia (Demarçay, Compt. rend. 1900, **130**, 1469; **131**, 343; 1901, **132**, 1484; Muthmann and Weiss, Annalen, 1904, **331**, 3; Feit, Z. anorg. Chem. 1905, **43**, 202, 267; Urbain, J. Chim. phys. 1906, **4**, 40, 105; James and Robinson, J. Amer. Chem. Soc. 1911, **33**, 1363; 1913, **35**, 754; Hughes and Hopkins, *ibid.* 1933, **55**, 3236).

(3) *Fractional Crystallisation of the Dimethyl Phosphates.*—Whereas the solubilities of the rare-earth salts usually increase from cerium to ytterbium the reverse is the case with the dimethyl phosphates. Moreover, the solubility differences are greater than are ordinarily met with so that they serve well for the separation of the terbium group (Morgan and James, *ibid.* 1914, **36**, 10; Jordan and Hopkins, *ibid.* 1917, **39**, 2614; Marsh, J.C.S. 1934, 1972; 1939, 554).

Numerous other salts have been recommended for separating the rare earths into the three main groups and mention may be made of the *bromates* (Jordan and Hopkins, *l.c.*), *formates* (Delafontaine, *l.c.*; Feit, *l.c.*) and *ethyl sulphates* (Urbain, Ann. Chim. Phys. 1900, [vii], **19**, 184).

Separation of the rare earths has been facilitated to some extent by the discovery that some of them can be reduced to the bivalent condition and that in this state the sulphates resemble those of the alkaline earths in being sparingly soluble in water. This is particularly useful in removing europium from samarium, gadolinium and terbium since electrolytic reduction of a solution of the chlorides in sulphuric acid leads to the precipitation of europous sulphate (Marsh, *l.c.*; Yntema, J. Amer. Chem. Soc. 1930, **52**, 2782).

Preparation of the Metal.—The first attempt to obtain gadolinium metal was made by Schumacher and Harris (*ibid.* 1926, **48**, 3108), who reduced the oxide with aluminium powder but found it impossible to remove the aluminium from the resulting alloy either by distillation or by treatment with potash. Fairly pure gadolinium has been obtained by electrolysis of a fused mixture of gadolinium, potassium and lithium chlorides in a graphite crucible which formed the anode, the cathode being a button of molten cadmium in a fluorite cup; the electrolyte was kept at a temperature of 625–675°C. A fusible alloy was produced with the cadmium from which the latter was removed by fractional distillation in a high vacuum (Trombe Compt. rend. 1935, **200**, 459; Bull. Soc. chim. 1935, [v], **2**, 660). Gadolinium has also been obtained by heating the chloride with alkali metal (Klemm and Bommer (Z. anorg. Chem. 1937, **231**, 138).

Physical Properties.—The relative abundance of the seven (?) isotopes of gadolinium 152, 154, 155, 156, 157, 158 is about 0·2, 1·5, 21, 23, 17, 23 and 16 respectively. The existence of the first two of these isotopes is doubtful (Aston, Nature, 1933, **132**, 930).

Much attention has been paid to the magnetic properties of the element. It has ferromagnetic and paramagnetic Curie points at 16° and 29·5°C. respectively, and at low temperatures its ferromagnetic properties are superior to those of iron. At 0° absolute the specific magnetisation is 253·5 C.G.S. units as compared with 221·7 for iron, while the atomic moments, expressed in Weiss magnetons, are 35·4 for gadolinium and 11 for iron. The magnetic moment of the $Gd^{\cdots}$ ion is 39·26 magnetons while that of the oxide Gd_2O_3 is 39·25; the moment of the sulphate $Gd_2(SO_4)_3,8H_2O$ is 39·28 (Urbain, Weiss and Trombe, Compt rend. 1935, **200**, 2132; Trombe, *ibid.* **201**, 652; Ann. Physique, 1937, [xi], **7**, 385; Cabrera, Compt. rend. 1937, **205**, 400; J. Chim. phys. 1939, **36**, 117; Néel, Z. Elektrochem. 1939, **45**, 378).

The reduction potential is −1·810 and the potential of metal formation is −1·955 (Noddack and Brukl, Angew. Chem. 1937, **50**, 362). In 0·1*N* solution of the chloride the transference number of gadolinium is 0·433 (Haas and Rodebush, J. Amer. Chem. Soc. 1933, **55**, 3238).

Spectra.—Like many of the rare-earth elements the emission spectrum of gadolinium is rich in lines, the chief ones in the arc spectrum being: 3082·0, 3646·2, 3671·25, 3719·5, 3768·4, 3796·45, 3814·0, 3852·5, 3916·6, 4037·35, 4063·5, 4130·4, 4184·3, 4262·1, 4342·2, 6996·8.

Some additional prominent lines in the spark spectrum are: 2904·7, 2955·5, 3350·5, 3422·5, 3585·0, 3664·6, 4251·8, 4436·2 (Albertson, Physical Rev. 1935, [ii], **47**, 370; 1936, [ii], **49**, 208; King, Astrophys. J. 1930, **72**, 221).

Gadolinium possesses the simplest absorption spectra of the rare-earth ions consisting of a number of extremely sharp lines mainly in the ultra-violet. In the case of $GdCl_3,6H_2O$ and $GdBr_3,6H_2O$ the spectra indicate that the 6 mol. of water are spaced symmetrically around the $Gd^{\cdots}$ ion and lie between it and the halogen ion (Spedding *et al.*, J. Amer. Chem. Soc. 1930, **52**, 3747; 1933, **55**, 497; Physical Rev. 1931, [ii], **38**, 2295; J. Chem. Physics, 1937, **5**, 33).

CHEMICAL PROPERTIES.—Hot water has no appreciable action on the metal though it slowly tarnishes in moist air; it is attacked by hydrochloric acid.

Conflicting results have been obtained in determining the basicity of gadolinium in relation to its neighbours in the rare-earth series. Sherwood and Hopkins (J. Amer. Chem. Soc. 1933, **55**, 3117) studying the precipitation by sodium nitrite give the order Sa>Eu>Gd, in agreement with Katz and James (*ibid.* 1914, **36**, 779) (hydrolysis of sulphates) and Brinton and James (*ibid.* 1921, **43**, 1451) (hydrolysis of carbonates). On the other hand, the last-named authors from experiments on the precipitation by ammonium hydroxide obtain the order Gd>Sa which agrees with the order Eu>Gd>Sa given by Britton (J.C.S. 1925, **127**, 2142). Brauner and Švagr (Coll. Czech. Chem. Comm. 1932, **4**, 49, 239) state that the basicity of the rare earths diminishes from La to Sa but increases again with Gd which has a basicity approaching that of lanthanum.

COMPOUNDS.

Gadolinium Oxide (gadolinia), Gd_2O_3.—Colourless, amorphous, hygroscopic powder absorbing carbon dioxide from air. It is prepared by igniting the hydroxide, nitrate, carbonate or oxalate; ignition of the sulphate needs a high temperature to expel the last traces of oxides of sulphur. Gadolinia is magnetic, its magnetic susceptibility increasing with decreasing temperature from about 130×10^{-6} at 20° to $279·0\times10^{-6}$ at −140°C. (Williams, Physical Rev. 1919, [ii], **14**, 348); its specific gravity at 15° is 7·407.

The hydroxide, $Gd(OH)_3$, is formed as a gelatinous precipitate, insoluble in excess of precipitant, when solutions of gadolinium salts are treated with alkali or ammonium hydroxide or sulphide; organic hydroxy acids hinder or prevent precipitation of the hydroxide. Like the oxide it absorbs carbon dioxide from the atmosphere.

Gadolinium Fluoride, GdF_3.—Addition of hydrofluoric acid to aqueous gadolinium sulphate yields the fluoride as a white gelatinous precipitate becoming granular on heating; it is somewhat soluble in hot hydrofluoric acid (Popovici, Ber. 1908, **41**, 634).

Gadolinium Chloride, $GdCl_3$.—Formed by heating the oxide or sulphide in dry hydrogen chloride, by the action of chlorine and a reducing agent on the oxide, by heating the oxide, sulphate or oxalate in the vapour of sulphur chloride or by heating the hydrated chloride in hydrogen chloride. It is best prepared by heating the oxide with excess of ammonium chloride to 200°, or higher, the residual ammonium salt being removed *in vacuo* at 300–320°C. (Reed, Hopkins and Audrieth, J. Amer. Chem. Soc. 1935, **57**, 1159; "Inorganic Syntheses," 1939, Vol. 1, p. 28; Jantsch *et al.*, Z. anorg. Chem. 1932, **207**, 353).

White, hygroscopic mass of monoclinic crystals, sp.gr. 4·52 at 0°; m.p. 609°±2° (Jantsch *et al.*, *l.c.*, 628°; Bourion, Ann. Chim. Phys. 1910, [viii], **21**, 74). It is soluble in water and concentration of the aqueous solution yields the hexahydrate $GdCl_3,6H_2O$ as deliquescent monoclinic crystals, sp.gr. 2·424. Gadolinium chloride forms double salts with platinic and auric chlorides.

When a slow current of air is passed over the molten anhydrous chloride there is produced an *oxychloride*, $GdOCl$, which is almost insoluble in water (Bourion, *l.c.*).

Gadolinium Bromide.—Both the anhydrous and hydrated salts closely resemble the corresponding chlorides and may be obtained in like manner. The melting-point of the former is not sharp but extends from 765 to 786°.

Gadolinium Iodide.—Pale lemon-yellow salt difficult to obtain pure. Formed by heating the anhydrous chloride at 600° in a stream of hydrogen iodide, it melts at 926°C. (Jantsch *et al.*, *l.c.*).

Gadolinium Chlorate, $Gd(ClO_3)_3,10H_2O$; **perchlorate**, $Gd(ClO_4)_3,8H_2O$; **bromate**,

$Gd(BrO_3)_3,9H_2O$;

iodate, $Gd(IO_3)_3,5\frac{1}{2}H_2O$; and **periodate**,

$GdIO_5,4H_2O$,

have also been prepared. The two last-named salts are insoluble in water (Sarkar, Bull. Soc. chim. 1926, [iv], **39**, 1390; Ann. Chim. 1927, [x], **8**, 207).

Gadolinium Sulphate, $Gd_2(SO_4)_3,8H_2O$.—Separates from a hot solution of the oxide in sulphuric acid as colourless monoclinic crystals isomorphous with the corresponding hydrated sulphates of the other rare earths; its sp.gr. at 14·6° is 3·01. The solubility in water decreases with increasing temperature being 3·98 g., $Gd_2(SO_4)_3$ per 100 g. H_2O at 0°C. and 2·26 g. at 34·4°.

Heating the octahydrate to 400° yields the anhydrous salt, sp.gr. 4·139 at 14·6°. Above 500° decomposition begins, while at 800–850° there is said to be produced an *oxysulphate*, $Gd_2O_2SO_4$.

Gadolinium Sulphite.—Hydrates with 11 and 12 mol. H_2O have been reported. The first is obtained by double decomposition between gadolinium nitrate and sodium sulphite while the second is formed by passing sulphur dioxide into an aqueous suspension of gadolinia until a clear solution results; alcohol is then added and the solution allowed to crystallise (Sarkar, *l.c.*).

Gadolinium Sulphide, Gd_2S_3.—Like the sulphides of the other rare earths it cannot be prepared in a wet way but is formed when hydrogen sulphide is passed over the heated sulphate. The resulting yellow solid has a density 3·8, is hygroscopic and is slowly decomposed by water.

Gadolinium Selenate.—The octahydrate, $Gd_2(SeO_4)_3,8H_2O$, is isomorphous with the corresponding sulphate and is formed when crystallisation takes place from aqueous solutions at 100°; at room temperature the decahydrate crystallises out.

The double salt, $Gd_2(SeO_4)_3 \cdot K_2SeO_4,4H_2O$, has also been made.

Gadolinium Acid Selenite,

$$Gd_2(SeO_3)_3 \cdot H_2SeO_3,6H_2O,$$

is obtained as an amorphous precipitate, becoming crystalline on standing, when selenious acid is added to the acetate.

Gadolinium Chromate.—Interaction of aqueous solutions of potassium chromate and gadolinium nitrate yields a gelatinous precipitate, slowly becoming crystalline, of a double salt, $K_2CrO_4 \cdot Gd_2(CrO_4)_3,7H_2O$. If the alkali chromate solution is saturated the precipitate corresponds to the formula

$$5K_2CrO_4 \cdot Gd_2(CrO_4)_3,10H_2O.$$

Gadolinium Nitrate, $Gd(NO_3)_3$.—A hexa- and penta-hydrate are known; the former is produced when the nitrate is crystallised from aqueous solution while the latter separates when conc. nitric acid is the medium. The hexahydrate forms deliquescent triclinic crystals, sp.gr. 2·332, m.p. 91°; it is soluble in water and alcohol. The pentahydrate yields prismatic crystals, m.p. 92°, sp.gr. 2·406. It is the least soluble in nitric acid of all the rare-earth nitrates (von Lang and Haitinger, Annalen, 1907, **351**, 450; Sarkar, *l.c.*).

Numerous double nitrates have been prepared, those with the bivalent metals magnesium and nickel having proved useful in the separation of gadolinium.

Gadolinium Orthophosphate,

$$GdPO_4,5\tfrac{1}{2}H_2O.$$

—Formed as a gelatinous precipitate, slowly becoming crystalline, when a conc. and slightly ammoniacal solution of disodium phosphate is added to gadolinium chloride solution.

Gadolinium Carbonate.—Carbon dioxide passed through a warm aqueous suspension of gadolinium hydroxide causes the appearance of small crystals which, dried at 100°, correspond to the basic carbonate $Gd(OH)CO_3,H_2O$. If passage of the gas be continued for a long time, larger crystals appear which apparently consist of the normal carbonate $Gd_2(CO_3)_3,13H_2O$.

Addition of potassium carbonate to a solution of a gadolinium salt precipitates a double carbonate, $H_2CO_3Gd_2(CO_3)_2 12H_2O$.

Gadolinium Formate, $Gd(HCOO)_3$.—Obtained by concentrating a solution of the hydroxide in dilute formic acid; the crystals when dried over potassium carbonate are anhydrous.

Gadolinium Oxalate, $Gd_2(C_2O_4)_3,10H_2O$.—Separates in monoclinic crystals from a solution in nitric acid. Sarkar states that addition of a conc. solution of potassium oxalate to one of gadolinium chloride yields a sparingly soluble precipitate of the double salt

$$KGd(C_2O_4)_2,4H_2O.$$

The *acetate, malonate, tartrate, citrate* and salts of many other organic acids are also known (Sarkar, *l.c.*).

Gadolinium Dimethyl Phosphate,

$$Gd(Me_2PO_4)_3.$$

—Obtained as colourless needles on crystallising a solution of gadolinia in dimethyl hydrogen phosphate. Its solubility decreases markedly with increasing temperature, being 37 g. per 100 g. H_2O at 0°, 24·2 g. at 25° and 6·7 g. at 95°. The salt tends to hydrolyse in aqueous solutions though this is not serious below 50° (Morgan and James, J. Amer. Chem. Soc. 1914, **36**, 10; Marsh, J.C.S. 1939, 554).

Gadolinium Acetylacetone,

$$Gd(C_5H_7O_2)_3,3H_2O.$$

—Separates as a sparingly soluble, crystalline precipitate when a slightly ammoniacal solution of acetylacetone is added to a neutral solution of gadolinium chloride. Recrystallised from chloroform and then from boiling alcohol it is obtained as rhombic crystals, m.p. 143·5–145° (Jantsch and Meyer, Ber. 1920, **53**, 1577; Sarkar, *l.c.*).

Gadolinium Platinocyanide,

$$2Gd(CN)_3 \cdot Pt(CN)_2,18H_2O.$$

—Red rhombic crystals with a green reflex resembling the isomorphous platinocyanides of yttrium and erbium; the corresponding double salts of the cerium group are yellow with a blue reflex.

Other complex cyanides which have been prepared are the **cobalticyanide,**

$$Gd_2[Co(CN)_6]_2,9H_2O,$$

the **ferrocyanide,** $KGd[Fe(CN)_6],5H_2O$, and the **ferricyanide,** $Gd[Fe(CN)_6],4\tfrac{1}{2}H_2O$.

Bibliography.—B. S. Hopkins, "Chemistry of the Rarer Elements," 1923; S. I. Levy, "The Rare Earths," London, 1924; J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. V, London, 1924.

G. R. D.

GAHNITE or ZINC-SPINEL. Zinc aluminate, $ZnAL_2O_4$, crystallised in the cubic system and belonging to the spinel group of minerals. According to the formula it contains 44·3% ZnO (35·6% Zn), but this is usually partly replaced isomorphously by ferrous oxide, manganous oxide and magnesia, whilst the alumina may be partly replaced by ferric oxide. The mineral usually occurs as grey or dark greenish-black, opaque octahedra. Sp.gr. 4·5–4·9; hardness 7½–8, n_D 1·805–1·818. It occurs as crystals embedded in talc-schist at Fahlun in Sweden, and more abundantly in crystalline limestone with other zinc ores (*willemite* and *franklinite*) at Franklin Furnace and Sterling Hill in New Jersey. It is also found at Bodenmais in Bavaria (with pyrrhotine), Massachusetts, Western Australia and a few other localities; and has also been observed in the muffles of zinc furnaces. The mineral was named in 1807 after the Swedish chemist, J. G. Gahn (1745–1818).

A blue gem spinel from Ceylon containing ZnO 18·21% replacing magnesia, and with sp.gr. 3·967, n_D1·7465, has been named *gahnospinel* (B. W. Anderson and C. J. Payne, Min. Mag. 1937, **24**, 547).

L. J. S.

GAHNOSPINEL *v.* GAHNITE.

GAHN'S ULTRAMARINE (Vol. II, 25*a*).

GAIZE (*v.* Vol. II, 146*b*).

GALACTAN - SULPHURIC ACID ESTER (*v.* Vol. II, 23*d*).

GALACTOCAROLOSE (this Vol., p. 58*a*).

GALACTOGEN (*v.* Vol. II, 302*d*).

GALACTOSE (Vol. II, 286*a*).

GALACTURONIC ACID (*v.* Vol. II, 297*d*).

GALAFATITE: An aluminium potassium sulphate found at Benahabux near Almeria and other places in Spain, where it occurs in parallel veins from 5 to 6 m. thick. It is white when pure, has a sp.gr. 2·75 and hardness 3·5. It is treated by calcination, followed by lixiviation with water, whereby a solution of potassium sulphate and a residue of nearly pure alumina are obtained. The calcined ore contains 60–70% of alumina and 25–30% of potassium sulphate (Preus, Eng. and Min. J. 1911, **91**, 261; J. Soc. Chem. Ind. 1911, **30**, 282). It is evidently a form of alunite (*q.v.*).

L. J. S.

"*Galalith.*" One of the early casein-formaldehyde plastics, still manufactured for buttons, handles, etc. (B.P. 24742, 1897).

GALAM BUTTER (*v.* Vol. I, 654*b*).

GALANGA ROOT is the rhizome of *Alpinia officinarum* Hance, a native of China, and is employed in the form of a decoction as a remedy for dyspepsia.

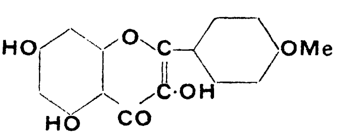
Galanga root was first examined by Brandes (Arch. Pharm. 1839, [ii], **19**, 52), and was subsequently studied by Jahns (Ber. 1881, **14**, 2385), Gordin (Dissert., Bern, 1897), Ciamician and Silber (Ber. 1899, **32**, 861) and Testoni (Gazzetta, 1900, **30**, ii, 327). These investigations demonstrated that it contains kaempferide, galangin and galangin monomethyl ether.

Kaempferide, $C_{16}H_{12}O_6$, yellow needles, m.p. 225°, is soluble in alkaline solutions with a yellow colour and its yellow solution in sulphuric acid shows a blue fluorescence.

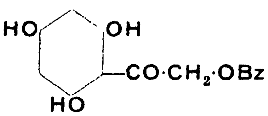
The following derivatives have been prepared: *Triacetyl-*, colourless needles, m.p. 193–194°, *tribenzoyl-*, m.p. 177–178°; *diethyl ether*, yellow needles, m.p. 137–139°; and *dibromo*-compound, yellow needles, m.p. 224–225° (decomp.).

With mineral acids in presence of acetic acid, kaempferide gives yellow crystalline oxonium salts, and with alcoholic potassium acetate forms a *monopotassium salt* which is decomposed by boiling water (Perkin and Wilson, J.C.S. 1903, **83**, 136).

Kaempferide is kaempferol 4′-methyl ether (I) (Herstein and von Kostanecki, Ber. 1899, **32**, 318) and this constitution has been confirmed by synthesis (Heap and Robinson, J.C.S. 1926, 2336) as follows: Condensation of benzoyloxyacetonitrile with phloroglucinol (Hoesch reaction) yields ω-benzoyloxyphloracetophenone (II) which, when heated with anisic anhydride and sodium anisate and the product hydrolysed, gives kaempferide (I).



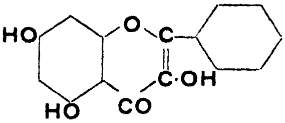
I.



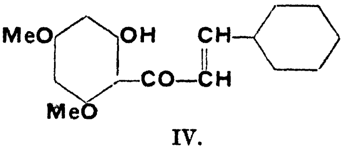
II.

Galangin, $C_{15}H_{10}O_5$, yellowish-white needles, m.p. 214–215°, is soluble in alkaline solutions with a yellow colour. With acetic anhydride it forms a *triacetyl* derivative, colourless needles, m.p. 142·5–143·5°, and with methyl iodide a *dimethyl ether*, m.p. 142°. It gives crystalline oxonium salts with mineral acids in the presence of acetic acid, and reacts with alcoholic potassium acetate to form *monopotassium galangin*, yellow needles (Perkin and Wilson, *l.c.*).

When fused with alkali, phloroglucinol and benzoic acid are produced; galangin is, therefore, 5:7-dihydroxyflavonol (III). It was first synthesised by von Kostanecki, Lampe and Tambor (Ber. 1904, **37**, 2803) by converting 2′-hydroxy-4′:6′-dimethoxy-chalkone (IV) into the corresponding flavanone, and the latter into its isonitroso-derivative. This compound, on boil-

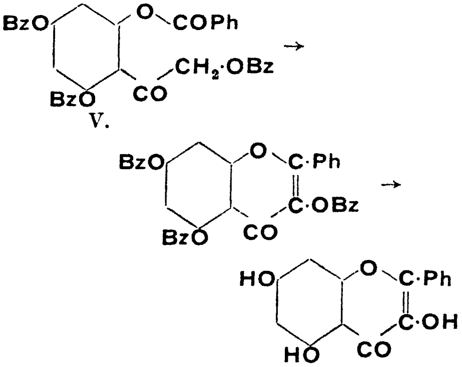


III.



IV.

ing with dilute sulphuric acid, gave 5:7-dimethoxyflavonol which yielded galangin on demethylation. Galangin has also been synthesised by the benzoylation of ω-benzoyloxyphloracetophenone (II), followed by hydrolysis of the product (Heap and Robinson, *l.c.*), and, less conveniently, by dehydrating ω-2:4:6-tetrabenzoyloxyacetophenone (V) by means of boiling acetic anhydride in presence of sodium acetate and hydrolysing the product (Chavan and Robinson, J.C.S. 1933, 368).


V.

Galangin dyes the following shades on mordanted woollen cloth:

Chromium.	Aluminium.	Tin.	Iron.
Olive-yellow.	Yellow.	Lemon-yellow.	Deep olive.

Galangin monomethyl ether, rectangular, yellow plates, m.p. 299°, is soluble in dilute aqueous potassium hydroxide to an intense yellow solution, and in sulphuric acid to a yellow solution exhibiting green fluorescence. It forms a *diacetyl*-derivative, very pale yellow needles, m.p. 175–176°, and a *dibromide*, yellow needles, m.p. 202°.

When oxidised in alkaline solution by air, galangin monomethyl ether is converted into phloroglucinol and benzoic acid, and is, therefore, galangin 3-methyl ether (Perkin and Allison, J.C.S. 1902, **81**, 472). Its synthesis was effected by benzoylation of ω-methoxyphloracetophenone and hydrolysis of the product (Kalff and Robinson, *ibid.* 1925, **127**, 181).

A. G. P. and E. J. C.

GALANGIN *v.* GALANGA ROOT.

GALAXITE. Manganese aluminate,

$MnAl_2O_4$,

belonging to the spinel group, found as small black grains in manganese ore in Alleghany Co., North Carolina, and named from the neighbouring town of Galax in Virginia. It has a red-brown streak and a mahogany-red colour by transmitted light; sp.gr. 4·234, hardness 7½, *n* 1·923 (C. S. Ross and P. F. Kerr, Amer. Min. 1932, **17**, 15).

L. J. S.

GALBANUM. This gum resin, which also contains an essential oil, is produced from *Peucedanum* (*Ferula*) *galbaniflua* and several other allied species of the *Umbelliferæ* indigenous to Persia. These plants flourish principally in Persia, although existing elsewhere.

The commercial resin, which is used only to a very limited extent in medicine, normally has the following characters:

Specific gravity	1·109–1·133 at 15·5°
Mineral matter	4–8%
Essential oil	5–12%
Resin soluble in alcohol	55–70%
Gum	20–25%
Acid value of resin	20–40
Ester value of resin	60–100

Rarely 20% of essential oil occurs in very soft types of the resin. Galbanum was included in the 1580 edition of the "Pharmacopœia Augustana" and in the 1589 edition of the "Dispensatorium Noricum." The essential oil is of a disagreeable odour, and has the following characters:

Specific gravity	0·915–0·955 at 15·5°
Optical rotation	−10° to +20°
Refractive index	1·4850–1·4960 at 20°

It contains pinene, nopinene, myrcene, cadinene, cadinol and probably a ketone of the formula $C_{10}H_{16}O$.

Most of the older statements as to the constituents of the resin itself are unreliable, but *umbelliferone* either in the free or the combined condition is present. The most recent work on this subject is that of Kunz and Wöldicke (Ber. 1937, **70** [B], 359). Apart from umbelliferone, *galbaresinic acid*, $C_{24}H_{30}O_5$ or $C_{23}H_{28}O_5$ is present. Traces of *galbanic acid*, $C_{15}H_{22}O_2$, are present, and at least two neutral lactones, both of which have the same formula $C_{24}H_{30}O_4$ or $C_{23}H_{28}O_4$. If powdered galbanum be boiled with hydrochloric acid under a reflux condenser for 15 minutes, the liquid cooled and filtered, and rendered alkaline with ammonia, the solution has a marked blue fluorescence.

E. J. P.

GALEGINE. Galegine was obtained by Tanret from *Galega officinalis* (Fam. Papilionaceæ).

Galegine, $C_6H_{13}N_3$, m.p. 60–65°, is optically inactive, forms hygroscopic crystals, readily soluble in H_2O and EtOH, insoluble in Et_2O,$CHCl_3$ and light petroleum; it takes up CO_2 from the air. The salts are crystalline, $B_2{\cdot}H_2SO_4$ is soluble in 23 parts of H_2O and 382 parts of 95% EtOH at 19°, the hydrochloride is hygroscopic, other known salts are the nitrate, oxalate, picrate, etc.; the dibenzoyl derivative forms needles, m.p. 95–96°.

Galegine yields on hydrolysis not methylpyrrolidine, as Tanret supposed (Compt. rend. 1914, **158**, 1182), but an unsaturated amine $C_5H_{11}N$, possibly the aminoamylene,

$$CMe_2{:}CH{\cdot}CH_2{\cdot}NH_2,$$

and Barger and White (Biochem. J. 1923, **17**, 827) suggest for galegine the constitution

$$CMe_2{:}CH{\cdot}CH_2{\cdot}NH{\cdot}C({:}NH)NH_2$$

They reduced the base catalytically to dihydrogalegine, which they synthesised from *iso*amylamine and cyanamide; oxidation with $Ba(MnO_4)_2$ furnished acetone and guanidinoacetic acid. Galegine gives Weyl's reaction with nitroprusside and a pale red coloration with diacetyl, showing the presence of a guanidine nucleus (Harden and Norris, J. Physiol. 1911, **42**, 332). These results were confirmed by

Späth and Prokopp (Ber. 1924, **57** [B], 474) and galegine was synthesised by Späth and Spitzy (*ibid.* 1925, **58** [B], 2273). For a later synthesis, *see* Ehrhart, Amer. Chem. Abstr. 1937, **31**, 5865.

For the microchemical identification of galegine, *see* Klein and Schlögl, *ibid.* 1932, **26**, 4413. The yield of the sparingly soluble sulphate (m.p. 227°) obtained by Tanret, Barger and White, and Späth and Prokopp was uniformly 0·5% of the seeds. The simplest method of extraction is that of Barger and White, avoiding organic solvents other than alcohol. Müller (Z. Biol. 1925, **83**, 239) extracts quantitatively by precipitation as picrate, and gives some biological details; on putrefaction hydroxydihydrogalegine is formed.

Galegine, being a guanidino-compound, it and its derivatives have been used experimentally and clinically as substitutes for insulin (*cf.* Müller and Reinwein, Arch. exp. Pathol. Pharmakol. 1927, **125**, 212; Reinwein, Münch. med. Woch. 1927, **74**, 1794; Chem. Zentr. 1928, II, 1456; Braun, J. Chem. Educ. 1931, **8**, 2175).

Schl.

GALENA (Ger. *Bleiglanz*; Fr. *Galène*). Native lead sulphide (**PbS**), the principal ore of lead (86·6%). It crystallises in the cubic system, and possesses three directions of perfect cleavage parallel to the faces of the cube. Well-developed crystals, with the form of the cube or cubo-octahedron, are not uncommon. The massive mineral is always readily recognised by its rectangular stepped cleavages with smooth and brilliant surfaces and a lead-grey colour; small broken fragments have the form of cubes or dice. Further, it can be readily scratched with a knife (hardness 2½) yielding a black powder, and it is very heavy (sp.gr. 7·5). Ore with a very fine-grained texture may present somewhat the appearance of steel.

The presence of small quantities of silver in galena is of importance; though usually not more than a few ounces per ton in amount, it may reach 1%. It is probably present in solid solution as silver sulphide, since argentite (*q.v.*) is isomorphous with galena. Examining polished surfaces of galena by reflected light under the high powers of a microscope, A. M. Finlayson (Quart. J. Geol. Soc. 1910, **66**, 319) was able to detect fine strings of native silver running along the cleavage cracks of the galena. This was, however, only detected in specimens taken from the higher levels within reach of surface waters; specimens taken from deeper levels, where there has been no secondary alteration, showed no native silver. F. N. Guild (Econ. Geol. 1917, **12**, 297) found that galena containing 0·10–0·35% silver shows definite spots of tetrahedrite and argentite; whilst specimens containing more silver show evidence of later addition of ruby-silver, etc., in the form of veinlets.

Galena occurs chiefly in veins traversing rocks of various kinds, and also filling cavities in limestone. It is abundant in all lead-mining districts, and by its alteration it gives rise to *cerussite*, *anglesite* and other secondary lead-bearing minerals. The use of galena for glazing pottery gave rise to the names "potters' ore," "alquifoux" (Fr.) and "archifoglio" (Ital.). The powdered mineral is used as a cosmetic by the natives of Nigeria.

L. J. S.

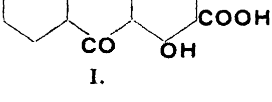
GALIPOT, Barras, Bordeaux or French turpentine, is the product of *Pinus maritima*, and to some extent of the so-called frankincense pine. It appears to consist of free acids closely related to pimaric acid.

GALIUM. The roots of various species of galium have been employed to some extent for dyeing red on aluminium mordant, and Bancroft, "Philosophy of Permanent Colours," London, 1813, Vol. II, p. 303, mentions six of these plants, the roots of which gave an excellent red in this manner. More especially he refers to the *Galium tinctorium*, the roots of which were employed by the French inhabitants of Canada to dye their cloths red.

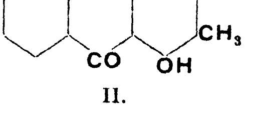
According also to Bancroft, the roots of the nearly allied species of *Asperula*, of which he specially mentions the *Asperula tinctoria* known as "Dyer's woodruff," were at one time used instead of madder for dyeing red.

The colouring matters present in plants of the tribe *Galieæ* of the *Rubiaceæ* have been investigated by Hill (Nature, 1934, **134**, 628), Richter (J.C.S. 1936, 1701) and Hill and Richter (Nature, 1936, **138**, 38; J.C.S. 1936, 1714; Proc. Roy. Soc. 1937, B, **121**, 547). The madder plant, *Rubia tinctorum*, belongs to this group, and examination of the related Bedstraws (*Galium*) has shown that purpurin-3-carboxylic acid occurs in the roots of members of the whole tribe *Galieæ*. Alizarin is found in significant amounts only in certain species, *e.g. Rubia tinctorum*, *Galium mollugo*, *G. erectum*; it is absent in the wild madder, *Rubia peregrina*, and only a trace occurs in *Galium verum*.

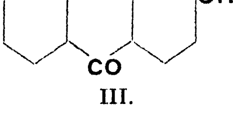
The three principal colouring matters, purpurin-3-carboxylic acid (I), rubiadin (II), and alizarin (III) occur in the plants as glycosides and these are isolated from the roots in the following manner:



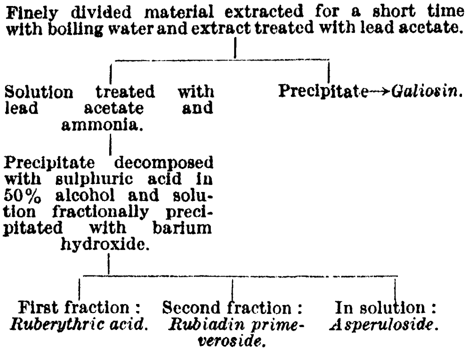
I.



II.



III.


Finely divided material extracted for a short time with boiling water and extract treated with lead acetate.

Solution treated with lead acetate and ammonia.

Precipitate→*Galiosin.*

Precipitate decomposed with sulphuric acid in 50% alcohol and solution fractionally precipitated with barium hydroxide.

First fraction: *Ruberythric acid.*

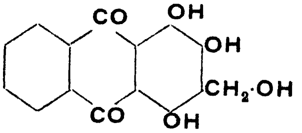
Second fraction: *Rubiadin primeveroside.*

In solution: *Asperuloside.*

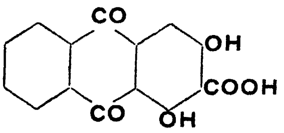
Galiosin, $C_{26}H_{26}O_{16},6H_2O$, was isolated from *Rubia tinctorum*, *R. peregrina*, *Galium verum* and *G. mollugo*, and its characteristic colour reactions were given by the other species from which purpurin-3-carboxylic acid was obtained. It forms yellow needles which decompose above 100° and dissolve in dilute alkalis with a deep orange coloration.

Galiosin is extremely unstable and is decomposed, for example, on standing with cold dilute hydrochloric acid or sodium carbonate solution, or by boiling for a few hours with either alcohol or water. When hydrolysed under very mild conditions with dilute acid, it yielded purpurin-3-carboxylic acid and a disaccharide identified as primeverose (6-β-*d*-xylosido-*d*-glucose). The constitution of the sugar was established by hydrolysing it to glucose and *d*(+)-xylose.

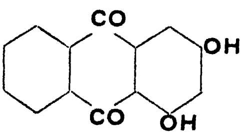
The structure of the aglycone, purpurin-3-carboxylic acid, was confirmed by synthesis. Condensation of purpurin with formaldehyde in the presence of sulphuric acid at 20° yields 3-hydroxymethylpurpurin (IV) which is converted into purpurin-3-carboxylic acid (I), m.p. 218–220° (decomp.), by oxidation with nitrososulphuric acid in the presence of boric acid at 145°.



IV.

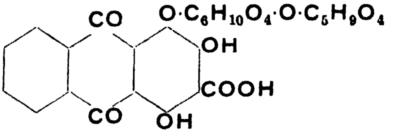


V.



VI.

Galiosin is reduced to *munjistin* (V) under extremely mild conditions, *e.g.* by treatment with colloidal palladium and hydrogen in cold dilute aqueous solution, the sugar residue being removed in the process. This reaction, together with the fact that galiosin resembles munjistin and xanthopurpurin (VI) in its colour reactions and dyeing properties, indicates that the sugar residue is in the 1-position:

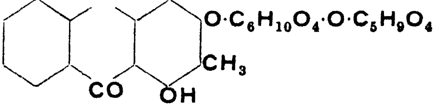


Galiosin.

Ruberythric acid, $C_{25}H_{26}O_{13},H_2O$, m.p. 257°, is the glycoside of alizarin (*v.* Vol. I, 216*c*).

Rubiadin primeveroside.—In addition to galiosin, the roots of *Galium verum* contain a considerable amount (0·14% of the fresh roots) of a rubiadin glycoside, $C_{26}H_{28}O_{13}$, pale yellow, parallel-sided plates, m.p. 248–250°. Very little alizarin glycoside is present in this plant.

When boiled with 0·4*N*-sulphuric acid for 6 hours, the rubiadin glycoside yielded *d*(+)-xylose and a product, yellow needles, m.p. 268°, which proved to be identical with the rubiadin-3-glucoside isolated by Schunck and Marchlewski (J.C.S. 1893, **63**, 969, 1137) from madder. Since the rubiadin glycoside gives red salts with alkalis, it is evident that one hydroxyl group in the anthraquinone nucleus is free, and therefore the pentose is attached to the glucose as a disaccharide. By analogy with galiosin it is probable that this *d*(+)-xylosido-glucoside is also a primeveroside:



Rubiadin primeveroside.

Rubiadin primeveroside was also isolated from *Galium mollugo*.

Since galiosin, ruberythric acid and rubiadin primeveroside are hydrolysed by the enzymes of *Primula officinalis* and *P. vulgaris*, it is concluded that the sugar residues are attached to the aglycones by linkages of the normal β-glucosidic type.

Asperuloside was recognised by the green colour produced on boiling with acid. This glucoside, isolated by Hérissey (J. Pharm. Chim. 1925, [viii], **2**, 177; Compt. rend. 1925, **180**, 1695; 1926, **182**, 865; 1927, **184**, 1674) from *Asperula odorata*, *Galium aparine* and *G. verum*, forms colourless needles, m.p. 126–127°, $[\alpha]_D$ −204·4°, *M*, 410. By hydrolysis with acids or emulsin, it yields 43–45% of dextrose and a brown precipitate of a decomposition product of the unknown aglucone (*asperuligenol*). Hérissey (Bull. Soc. Chim. biol. 1926, **8**, 1208) considers that asperuloside is probably identical with the rubichloric acid obtained from madder root by Rochleder (Annalen, 1851, **80**, 321).

A. G. P. and E. J. C.

GALIOSIN, *v.* Galium.

GALIPINE, GALIPOLINE, GALIPOIDINE (*v.* Vol. III, 462*d*, 463*a*).

GALLACETOPHENONE,

$$C_6H_2(OH)_3{\cdot}CO{\cdot}CH_3.$$

Made by condensation of pyrogallol and acetic acid. Has been used as a mordant dyestuff under the name of *Alizarine Yellow* C.

GALLIC ACID, 3:4:5-*Trihydroxybenzoic acid*, $C_6H_2(OH)_3COOH$, discovered by Scheele in 1786 and its structure elucidated in 1834 by Pelouze (Ann. chim. Phys. 1833, [ii], **54**, 350; Annalen, 1834, **10**, 158), occurs widely distributed in many plants rich in tannin and as a product of fermentation (Freudenberg, "Die Chemie der natürlichen Gerbstoffe," Berlin, 1920; E. Fischer *et al.*, Ber. 1912, **45**, 929; 1914, **47**, 2495; 1918, **51**, 1772; 1919, **52** [B], 183). Thus, for example, it may be obtained from the Aleppo gall (Dizé, Gren's J. d. Physik, 1793, **7**, 401); from the acorn of *Quercus aegilops* L. (Stenhouse, Annalen, 1843, **45**, 15); from willow bark (Powarnin, Krassin and Powarnin, Chem. Zentr. 1914, I, 1510); from the leaves of *Coriaria japonica* A. Gray (U. T. Kariyone, K. Kasiwagi and S. Mizutani, J. Pharm. Soc. Japan, 1937, **57**, 182); from Chinese tea (Hlasiwetz and Malin, Annalen, 1867, **142**, 234); as the methyl ester from the fruit of *Cæsalpinia brevifolia* Baill. (Nierenstein. Chem. Zentr. 1905, II, 527); from the bark of *Hamamelis virginica* L. (Grüttner, Arch. Pharm. 1898, **236**, 293) and from Chinese galls (Feist and Haun, Chem.-Ztg. 1912, **36**, 1202).

It is obtained from tannin, by hydrolysis and by fermentation (Nierenstein, Chem.-Ztg. 1909, **33**, 126; Ber. 1910, **43**, 628; Sisley, Bull. Soc. chim. 1909, [iv], **5**, 730; Strecker, Annalen, 1852, **81**, 249; 1854, **90**, 331; Fernbach, Compt. rend. 1900, **131**, 1214; Grüttner, Arch. Pharm. 1898, **236**, 313). It has been formed by heating 3:5-dibrom-4-hydroxybenzoic acid with barium hydroxide and water at 175° (Bayer & Co., G.P. 249939, Chem. Zentr. 1912, II, 655).

Preparation.—Gallic acid is prepared by the mould fermentative fission of tannin (Scheele and Steer, J.C.S. 1856, **8**, 482). Willstein (*ibid.* 1853, **5**, 435) recommends an addition of yeast for the working of Chinese galls. The acid may be isolated from the mother liquor as the lead salt (Heinemann, Chem. Zentr. 1901, II, 1286). M. Nazarento (J. Appl. Chem. Russia, 1937, **10**, 166) gives a method for obtaining the acid in a 70% yield by hydrolysing the aqueous extract of tannin-containing plants with $NaOH$. The technical methods of preparation are discussed by I. Takino (J. Pharm. Soc. Japan, 1929, **49**, 1–59).

Physical Properties.—Gallic acid exists in two polymorphic forms (E. Lindpaintner, Mikrochem. 1939, **27**, 21). It is soluble in 3 parts of boiling water; 132 parts water at 12·5°; 4·5 parts absolute alcohol; 40 parts ether; 3·4 parts acetone and 12 parts ethyl acetate; insoluble in chloroform and benzene (Rosenheim and Schidrowitz, J.C.S. 1898, **73**, 882). It crystallises from water in monoclinic prisms with $1H_2O$ which it loses above 100° and melts at 238–240° (Perkin and Wood, *ibid.* 1898, **73**, 376; S. Hirano, J. Soc. Chem. Ind. Japan, 1939, **42**, Suppl. binding 26). d_4, solid, 1·694 (Schröder, Ber. 1879, **12**, 1612; 1880, **13**, 1074). Electrical dissociation constants by potentiometric titration and corrected for interionic attractions $K_1=4{\cdot}63\times10^{-5}$; $K_2=1{\cdot}41\times10^{-9}$ at 30° (C. Abichandani and S. Jatkar, J. Indian Inst. Sci. 1938, **21A**, 417). The acid is distinctly tetrabasic, as shown by electrometric titration (S. Sunthankar and S. Jatkar, *ibid.* 1938, **21A**, 209; Hans Schweitzer, Collegium, 1933, 149). Raman spectra (B. Susz, S. Fried and E. Briner, Helv. Chim. Acta. 1936, **19**, 1359). Exchange experiments with heavy water (F. Münzberg, Z. physikal. Chem. 1936, [B] **33**, 23). Effect of colloids on the solubility in water (L. Steenhuisen, Pharm. Weekblad, 1930, **67**, 1269).

Chemical Properties.—Gallic acid decomposes into CO_2 and pyrogallol by dry distillation (Bracannot, Annalen, 1832, **1**, 26; Pelouze, *ibid.* 1834, **10**, 159; Liebig, *ibid.* 1857, **101**, 48); by heating with 3 parts water under pressure at 200° (De Luynes and Esperandieu, Compt. rend. 1865, **61**, 489); by heating with glycerin (Thorpe, Pharm. J. 1881, [iii], **11**, 990), or with 2 parts aniline (Cazeneuve, Bull. Soc. chim. 1892, [iii], **7**, 549; 1896, [iii], **15**, 72; von Hemmelmayr, Monatsh. 1911, **32**, 790; 1913, **34**, 372).

Oxidation.—An alkaline solution of gallic acid absorbs oxygen from the air, forming a dark red solution (Bückner, Annalen, 1845, **53**, 369; Liebig, *ibid.* 1851, **77**, 111; Vaukel, Z. angew. Chem. 1903, **16**, 391; Schewket, Biochem. Z. 1913, **54**, 277). In the presence of air, at −5° to +5° and 2–3 mol. of alkali, gallic acid forms galloflavin (Bohn and Graebe, Ber. 1887, **20**, 2328). Gallic acid on oxidation with nitric acid (Schiffer, *ibid.* 1892, **25**, 722); chlorine, or $CuSO_4$ and alkali yields oxalic acid as the main product (Böttinger, Annalen, 1890, **257**, 248; 1890, **260**, 337; Biétrix, Compt. rend. 1896, **122**, 1545); with conc. sulphuric acid 1:2:3:5:6:7-Hexadroxy anthraquinone (rufigallic acid) is obtained (Robiquet, Annalen, 1836, **19**, 204). Ellagic acid is the product obtained by oxidising with persulphates in the presence of acetic and sulphuric acids (Perkin, J.C.S. 1905, **87**, 1412; 1906, **89**, 252); with $KMnO_4+H_2SO_4$ (Oser and Flögl, Ber. 1876, **9**, 135); with

$$Fe_2(SO_4)_3+H_2SO_4$$

(Bleuler and Perkin, J.C.S. 1916, **109**, 541); with iodine and water (Griessmayer, Annalen, 1871, **160**, 55); and with $KClO_3+HCl$ (Buschiyew, Chem. Zentr. 1910, I, 1011); with hydrogen peroxide it yields aconitic acid (Kariyone, Kasiwagi and Mizutani, J. Pharm. Soc. Japan, 1937, **57**, 182). With ferric salts the oxidation product forms a black blue precipitate (Barreswil Compt. rend. 1844, **17**, 739; 1844, **17**, 1064; Wackenroder, Annalen, 1840, **31**, 78; Arch. Pharm. 1841, **77**, 269). Pupurogallincarboxylic acid and in some cases flavellagic acid are obtained by electrolytic oxidation of gallic acid (A. Perkin and F. Perkin, J.C.S. 1904, **85**, 246; 1908, **93**, 1186).

Reduction.—Gallic acid is only appreciably reduced in alkaline solution, benzoic acid being produced (Guignet, Compt. rend. 1891, **113**, 200; Gardner and Hodgson, J.C.S. 1909, **59**, 1819).

Halogenation. — Chlorination in chloroform yield a mixture of dichlorogallic acid and trichloropyrogallol (Biétrix, Bull. Soc. chim. 1896, [iii], **15**, 904). Both mono- and di-bromogallic acid are produced by bromination under various conditions (Hlasiwetz, Annalen, 1857, **142**, 250; Grimaux, Compt. rend. 1867, **64**, 976; Biétrix, Bull. Soc. chim. 1892, [iii], **7**, 412; 1893, [iii], **9**, 241; Etti, Ber. 1878, **11**, 1882). Iodine acts as oxidant (*see above*).

Gallic acid condenses with many aryl hydroxy compounds (Noelting and Meyer, *ibid.* 1897, **30**, 2591; Graebe and Eichengrün, Annalen, 1892, **269**, 313; G.P. 49149); while $HCHO$ in the presence of HCl yields four different 2:2'-methylene-digallic acids (Möhlau and Kahl, Ber. 1898, **31**, 259; Kleeberg, Annalen, 1891, **263**, 285; Nierenstein and Webster, Ber. 1908, **41**, 81). Gallic acid may be successfully acetylated to triacetyl gallic acid with either acetyl chloride or acetic anhydride (Schiff, Annalen, 1872, **163**, 210; Böttinger, Ber. 1884, **17**, 1503; Sisley, Bull. Soc. chim. 1894, [iii], **11**, 565; Reychler, Chem. Zentr. 1908, I, 1042; F. Chattaway, J.C.S. 1931, 2495).

Gallic acid and its derivatives undergo condensations with nitrosodialkylanilines (Frdl. I, 267; II, 158, 167; IV, 485, 506; Chem. Zentr. 1910, I, 391; Houben, Ber. 1913, **46**, 3992) and with quinonechloroimine (Chem. Zentr. 1912, I, 180) to form dyestuffs of the oxazine or gallocyanine groups. It also condenses with *o*-nitrosonaphthols or *o*-aminonaphthols to form brown dyestuffs used in tanning (Frdl. IV, 504).

Detection and Estimation.—For colour reaction with iron salts, see *Chemical Properties*, also Weinland and Binder (Ber. 1912, **45**, 151). In presence of conc. sulphuric acid, alkaloids containing a methylene dihydroxy group exhibit a blue or green coloration on an alcoholic solution of gallic acid (Labat, Bull. Soc. chim. 1909, [iv], **5**, 742). A solution of KCN [1:30] produces a ruby-red coloration (Griggi, Boll. Chim. farm. 1898, **38**, 5; Sanchez, Bull. Soc. chim. 1911, [iv], **9**, 1058). An alkaline lead solution shaken with gallic acid in the presence of air produces a red colour (Spica, Gazzetta, 1901, **31**, II, 206), but if the lead is in excess the colour is green (Schewket, Biochem. Z. 1913, **54**, 280). For further colour reactions, *see* J. Quastel (Analyst, 1931, **56**, 311), S. A. Celsi (Rev. Centro estud. farm y. bioquím, 1928, **16**, 642) and Böttinger (Annalen, 1890, **256**, 341; J.S.C.I. 1890, **9**, 450). A microchemical reagent consisting of formol and HCl gives a micro-crystalline solid with gallic acid (L. Rasi and S. Celsi, Anales farm. bioquím, 1931, **2**, 40). Assay for purity of gallic acid is given in "Deutsches Arzneibuch," 6th ed., Berlin, 1926, 20.

Gallic acid has been estimated by the iodometric method (Gardner and Hodgson, Proc. Chem. Soc. 1908, **24**, 273; Dabvi, J. Indian Inst. Sci. 1931, **13A**, 193; Spica, Gazzetta, 1901, **31**, ii, 201; Harnack, Arch. Pharm. 1896, **234**, 537; Buchner, Annalen, 1845, **53**, 537; Hinsdale, Chem. News, 1891, **64**, 51; Dreaper, J.S.C.I. 1893, **12**, 412; Chem. News, 1904, **90**, 111; Jean, J.S.C.I. 1900, **19**, 382); by precipitation as bismuth subgallate (M. Hirsch, Chem.-Ztg. 1927, **51**, 718); by using Nessler's reagent (M. Goswami and A. Shaha (J. Indian Chem. Soc. 1937, **14**, 208); by neutralisation with alkali (Procter and Bennett, J.S.C.I. 1906, **25**, 251).

Salts of Gallic Acid.—Gallates of the metals are in general produced by the reaction of gallic acid with an oxide or hydroxide of a metal with a higher atomic number than 21 (Hans Schmidt (to Winthrop Chemical Co.) U.S.P. 1889383, Nov. 29, 1933; Büchner, Annalen, 1845, **53**, 175). "*Dermatol,*" *q.v.*, is bismuth subgallate and "*Airol,*" *q.v.*, is bismuth oxi-iodo-gallate. "*Gallogen* (*gallol*)," is the aluminium salt and used as an antiseptic astringent.

Uses.—Gallic acid is employed as photographic developer, in the manufacture of inks, preparation of dyestuffs and in medicine (G. Cohn in F. Ullmann, "Enzyklopädie der technischen Chemie," 2nd ed., Vol. V (Berlin, Wien, 1930), p. 469).

GALLISIN (*v.* Vol. II, 299*a*).

GALLIUM. Atomic weight 69·72 (69·74, Lundell and Hoffmann, 1935), atomic number 31, isotopes 69 and 71.

Predicted by Mendeléef and called by him eka-aluminium, gallium was discovered by Lecoq de Boisbaudran in 1875 during the spectroscopic examination of material isolated from the zinc blende of Pierrefitte in the Pyrenees. Although always occurring in minute quantities it is widely distributed in nature and, as might be expected, is often found associated with aluminium in clays, felspars, nephelines, etc. It is frequently a constituent of zinc blendes while it may also accompany iron, manganese and chromium in their ores; hence it has often been detected in commercial samples of these metals. The richest mineral source of the element is *germanite* (*q.v.*), a copper sulphide ore found in South-West Africa which may contain 0·5–0·7% of gallium. It is found in the ash of many coals in amounts up to 0·05% while in flue dusts an enrichment may take place, samples containing up to 2% having been obtained (Goldschmidt and Peters, Nachr. Ges. Wiss. Göttingen, 1931, 165; 1933, 371; Ramage, Nature, 1927, **119**, 783; Morgan and Davies, Chem. and Ind. 1937, **56**, 717).

At present the only source being worked for gallium is the rhenium-rich copper schist of Mansfeld. The aluminium phosphate residues occurring during the isolation of molybdenum and rhenium from this schist are dissolved in caustic soda and the solution carefully acidified with sulphuric acid when a precipitate consisting of basic sulphates and phosphates of aluminium and tin is obtained; this may contain upwards of 7% of gallium. The precipitate is dissolved in 4*N*-sulphuric acid and the solution submitted to fractional hydrolysis by adding water or, better, sodium sulphite. Gallium accumulates in the first fractions and these are again taken up in sulphuric acid, the solution now being treated with hydrogen sulphide under pressure to remove molybdenum and tin. The filtered liquor is then made strongly alkaline and the metal extracted electrolytically (Feit, Angew. Chem. 1933, **46**, 216).

In the further purification of the metal one or more of the following operations are used: (*a*) conversion into the chloride and extraction of this from $6N\text{-}HCl$ with ether; after removing the solvent the dilute solution of the residue is treated successively with hydrogen sulphide to remove heavy metals and excess sodium hydroxide to remove iron; (*b*) crystallisation of the alum, $(NH_4)Ga(SO_4)_2,12H_2O$; (*c*) fractional distillation of the chloride or bromide; (*d*) fractional crystallisation of the metal.

Physical Properties.—Gallium is a bluish-white diamagnetic metal melting at 29·78° to a lustrous silvery-white liquid the boiling-point of which is estimated to be about 2,300° abs.; the liquid shows a great tendency to superfusion. Two isotopes ^{69}Ga and ^{71}Ga are known, the relative abundance being 1·6:1·0 from which, assuming a packing fraction of $-9{\cdot}8\times10^{-4}$, an atomic weight of 69·71 is obtained. At temperatures removed from the melting-point gallium is hard and brittle though at room temperature it may be rolled into thin films; it marks paper with a grey streak and its hardness on the Moh scale is given as 1·5 (Rydberg) or 2–3 (Einecke). The density of the solid is 5·904 and of the liquid 6·095, the dilation on solidification being 0·00531 c.c. per g. The compressibility at 20° is $2{\cdot}09\times10^{-6}$, approximately half that for the liquid $(3{\cdot}97\times10^{-6})$. The latent heat of fusion $=-19{\cdot}16$ g.-cal.; specific heat between 0° and 16° $=0{\cdot}0887$ while that of the liquid is 0·0977; atomic heat $\sim 6{\cdot}25$. The mean coefficient of expansion (α) over the temperature range −78·3 to 18° is $5{\cdot}3\times10^{-5}$ and for the range 32·8–310° is $11{\cdot}87\times10^{-5}$.

The specific resistance of solid gallium is nearly twice that of the liquid, $\rho(0^\circ)=53{\cdot}0\times10^{-6}$, $\rho(30{\cdot}3^\circ)=27{\cdot}2\times10^{-6}$; Hall effect $=-6{\cdot}3\times10^{-4}$. At temperatures near the absolute zero the metal becomes superconducting.

Spectra.—In the X-ray spectrum the chief lines of the K series are $\alpha_1=1{\cdot}350$A, $\alpha_2=1{\cdot}34087$A, $\alpha_3=1{\cdot}33186$A, $\beta_1=1{\cdot}20543$A, $\beta_2=1{\cdot}1938$A, $\beta\gamma=1{\cdot}1959$A. The critical K absorption line is 1·1902A while the wave-length of the main K absorption edge is 1·1925A.

Both the arc and the spark spectra of gallium contain a number of intense lines suitable for purposes of detection; the most persistent lines are the two violet ones 4172·05 and 4033·03. The spectral series have been studied by Rydberg (K. Svenska Vet. Akad. Handl. 1890, **23**, No. 11), Paschen and Meissner (Ann. Physik, 1914, (4), **43**, 1223), absorption spectra, Grotrian (Z. Physik, 1923, **12**, 218; **18**, 169), X-ray spectra, Gwinner (*ibid.* 1938, **108**, 523); *see also* Fowler, "Report on Series in Line Spectra," London, 1922.

Crystal Structure of Gallium.—Orthorhombic with three different axes: $a=4{\cdot}5167$, $b=4{\cdot}5107$, $c=7{\cdot}6448$, $a{:}c$ 1·6926. Each atom is surrounded by seven others, one at 2·43 and two each at 2·70, 2·73 and 2·79A. This structure consists either of deformed hexagonal rings or possibly contains Ga_2 molecules (Bradley, Z. Krist. 1935, **91**, 302).

Chemical Properties.—The metal is stable in dry air but slowly tarnished in moist air or oxygen, the action proceeding more rapidly in the liquid phase. It does not decompose water although with caustic alkalis hydrogen is slowly evolved. Of the mineral acids concentrated hydrochloric acid alone attacks it to any appreciable extent in the cold. The action of nitric acid is comparatively slow even on warming for, like iron and aluminium, the metal acquires a certain degree of passivity; this is due to the resistant film formed under the action of oxidants. With liquid gallium the film is particularly tenacious and being fairly elastic is not easily perforated. Halogens attack the metal with vigour and the evolution of light and heat, although in the case of iodine warming is necessary to initiate the reaction.

Two classes of compounds are known in which gallium is respectively bivalent and trivalent; in addition there is also evidence of univalent derivatives.

Alloys.—Numerous binary and a lesser number of ternary, quaternary and even quinternary combinations have been produced some of which are liquid at room temperatures. Copper-gallium alloys resemble the brasses of aluminium, indium and tin. A little gallium increases both the strength and hardness of copper but the electrical conductivity is considerably decreased. A higher gallium content renders the alloys brittle so that they cannot be turned; this applies also to silver and zinc alloys. On the other hand gallium-magnesium alloys are easily turned or rolled while they may possess a hardness up to 50 Brinell. With aluminium, indium and tin there are formed low melting alloys; the eutectic with tin contains 8 atomic per cent. of this metal and melts at 18°. Addition of indium lowers the melting-point still further so that an alloy of 60% Sn, 30% Ga and 10% In has been recommended to replace mercury.

Uses.—Gallium has been used to some extent in thermometry, fused quartz being used instead of the glass of ordinary thermometers; temperatures up to 1,000° may be measured (Boyer, J. Opt. Soc. Amer. 1926, **13**, 117; *cf.* F.P. 610192; G.P. 453184). Mercury may also be replaced by $Ga\text{-}Al$ alloy in ultra-violet ray lamps, the therapeutic effect being further increased by small additions of cadmium, bismuth or mercury (G.P. 217951). Other suggested uses are in radio valves (U.S.P. 1866195), as a liquid seal in strongly heated apparatus which is being evacuated (G.P. 562212) and for coating optical mirrors.

Organic gallium salts also exert some curative action in experimental syphilis and trypanosomiasis (Levaditi, Bardet, Tchakirian and Vaisman, Compt. rend. 1931, **192**, 1142).

Compounds of Gallium.

Gallium and Halogens.

Gallium trifluoride, GaF_3.—White powder, subliming at 950°, obtained by heating ammonium gallifluoride, $(NH_4)_3GaF_6$, in nitrogen or fluorine at 250–400°. It is insoluble in water but dissolves in hydrofluoric acid and concentration of this solution leads to the formation of the crystalline trihydrate, $GaF_3,3H_2O$, which may also be prepared by dissolving the metal or oxide in excess HF.

The hydrate is perceptibly soluble in hot water and easily dissolves in dilute hydrochloric acid; when heated to 140° *in vacuo* the water of crystallisation is slowly expelled. Extraction of the trihydrate with liquid ammonia yields the triammoniate $GaF_3{\cdot}3NH_3$; the existence of a diammoniate is also indicated (Klemm and Kilian, Z. anorg. Chem. 1939, **241**, 93).

White double fluorides of the cryolite type, R_3GaF_6 (R=alkali metal or NH_4) have been made by dissolving stoichiometric amounts of the necessary fluorides, oxides or carbonates in HF and evaporating. The ammonium compound when gently heated forms $(NH_4)_2GaF_5$ and $(NH_4)GaF_4$ while $Ga(NH_3)F_2$ and $Ga(NH)F$ are produced at 220° and 400° respectively (Pugh, J.C.S. 1937, 1046, 1959; Hannebohn and Klemm, Z. anorg. Chem. 1936, **229**, 337; Henkel, Angew. Chem. 1934, **47**, 726; Johnson and Parsons, J. Amer. Chem. Soc. 1932, **54**, 2588; Aston, Nature, 1923, **112**, 449; Einecke, " Das Gallium," Leipzig, 1937).

Gallium trichloride, $GaCl_3$.—Prepared by the action of chlorine or hydrogen chloride on the metal or by heating the oxide in carbon tetrachloride; if the stream is sufficiently rapid gallium may take fire in the halogen, burning with a pale blue flame. The chloride is purified by fractional distillation, first in air and then *in vacuo*; colourless needles, m.p. 78°, b.p. 205°/755 mm. (Klemm and Tilk, Z. anorg. Chem. 1932, **207**, 161), 201·3° (Fischer and Jübermann, *ibid.* 1936, **227**, 227). Heat of formation at 20°=125 kg.-cal.; density of solid d_4^{25} 2·47; of the liquid d 2·063–0·00205(t−78°). Vapour density measurements indicate that just above the boiling-point the chloride is bimolecular (Ga_2Cl_6) while at 440° dissociation into simple molecules is complete; at 1,000° decomposition into $GaCl_2$ becomes evident. Gallium trichloride is very hygroscopic and easily hydrolysed; it fumes in damp air and dissolves in water with the evolution of heat forming a clear solution having an acid reaction and from which, on long standing, crystalline oxychlorides may be deposited; one such compound isolated by de Boisbaudran had the composition

$$Ga_2Cl_6,12H_2O,2Ga_2O_3,H_2O.$$

The aqueous solution loses hydrochloric acid on evaporation and a gel is produced. Unlike aluminium chloride, gallium chloride is freely soluble in ether and is almost completely extracted from solutions in 6*N*-hydrochloric acid by this solvent. No derivatives corresponding to the gallihexafluorides are known but Kraus and Toonder (Proc. Nat. Acad. Sci. 1933, **19**, 298) have obtained NH_4GaCl_4 by acting on trimethylgallium ammine, Me_3GaNH_3, with hydrogen chloride. For ammoniates of $GaCl_3$, *see* Klemm, Tilk and Jacobi (Z. anorg. Chem. 1932, **207**, 187).

Gallium dichloride, $GaCl_2$.—Prepared by heating gallium with its trichloride at 200° or by incomplete chlorination of the metal and distilling the colourless, strongly refracting liquid in carbon dioxide. White crystals, m.p. 164°, b.p. 535°; in common with other gallium halides it exhibits to a marked degree the phenomenon of supercooling. The dichloride is deliquescent, the crystals dissolving to a colourless solution which, on dilution, deposits a brown precipitate possessing reducing properties; this precipitate slowly becomes colourless and dissolves, probably as an oxychloride of trivalent gallium. The action of water on the dichloride always leads to the evolution of a gas, presumably hydrogen, but which, from its peculiar odour and action on test papers impregnated with silver or lead salts, was thought by de Boisbaudran to be a gallium hydride. Gallium dichloride does not yield ammoniates but with liquid ammonia at −78° it forms $GaCl_3,3NH_3$ and Ga (de Boisbaudran, Compt. rend. 1881, **93**, 294, 329; 1882, **95**, 18; Nilson and Pettersson, Z. physikal. Chem. 1888, **2**, 657; Dennis and Bridgman, J. Amer. Chem. Soc. 1918, **40**, 1531; Richards *et al.*, *ibid.* 1919, **41**, 500; Bowden and O'Connor, Proc. Roy. Soc. 1930, A, **128**, 317; Klemm and Tilk, Z. anorg. Chem. 1932, **207**, 161, 177; Fischer and Jübermann, *ibid.* 1936, **227**, 227; Roth and Büchner, Z. Elektrochem. 1934, **40**, 87).

Gallium monochloride, $GaCl$.—Vapour density measurements on gallium dichloride above 1,000° indicate a certain degree of dissociation into the monochloride while a study of the spectra of gallium halides shows the presence of band systems resembling those for $InCl$, $InBr$ and InI (Miescher and Wehrli, Helv. Phys. Acta, 1933, **6**, 458; 1934, **7**, 331).

Gallium tribromide.—Prepared by passing nitrogen laden with bromine vapour over the metal and purified by sublimation under low pressure and at about 100°. Colourless hygroscopic needles soluble in a little water to a clear solution having an acid reaction; m.p. 121·5° (122·5°; 124·5°), b.p. 279°/750 mm.; d^{120} 3·69, $d_{\text{liq.}}$ 3·138–0·0029(t−125°) (Fischer and Jübermann, *l.c.*; Klemm *et. al.*, *l.c.*; Johnson and Parsons, J. Physical Chem. 1930, **34**, 1210).

The tribromide forms a number of ammoniates of which the hexammine, $GaBr_3,6NH_3$, is stable in dry air at 18°; in the presence of moisture an exchange of NH_3 for H_2O takes place.

Gallium dibromide.—Less volatile than the dichloride, it is formed by the action of bromine on excess of the metal.

Gallium triiodide.—At ordinary temperatures iodine acts only slowly on gallium but combination takes place readily on warming. The triiodide is best prepared by heating equivalent quantities of the elements in an evacuated flask, the product being purified by sublimation under reduced pressure. It forms pale, lemon-yellow, hygroscopic crystals, readily soluble in, and hydrolysed by, water, m.p. 212° (213·5°, 210°), b.p. 346°; d_4^{25} 4·15, $d_{\text{liq.}}$ 3·60–0·00224(t−211°).

Of its ammoniates the monammine melts at 140° while the hexammine is stable in air at room temperature although very sensitive to moisture.

Gallium diiodide.—Light yellow crystals melting to a volatile, easily supercooled, red liquid; it is obtained similarly to the other dihalides.

Gallium perchlorate, chlorate, iodate and oxyiodate have also been made (Neogi and Nandi, J. Indian Chem. Soc. 1937, **14**, 492; Foster, J. Amer. Chem. Soc. 1939, **61**, 3122).

GALLIUM AND OXYGEN.

Gallium sesquioxide, Ga_2O_3. — When strongly heated in air or oxygen gallium burns with a violet flame, producing the sesquioxide which is usually prepared by thermal decomposition of the salts or by dehydration of the hydrate above 900°. The latter retains water tenaciously while, moreover, the oxide is hygroscopic unless heated to 1,200°; it is then insoluble in alkalis and only slowly so in mineral acids other than hydrofluoric. The melting-point is given as 1,740° by Wartenburg and Reich (Z. anorg. Chem. 1932, **207**, 1) and as being above 1,900° by Centola (Amer. Chem. Abstr. 1936, **30**, 4386). Like alumina it exists in several modifications; the oxide (α-Ga_2O_3) prepared at 430° possesses a structure similar to corundum and this changes at 625° to β-Ga_2O_3 which is monoclinic or rhombic and is stable up to the melting-point; density of α-form 6·44 and of β-form 5·88. Addition of certain oxides such as those of **Ti**, **Mn**, **Pt** and **Cr** induces fluorescence or phosphorescence in gallium oxide when it is heated in the oxy-hydrogen flame or in a cathode-ray furnace (Tiede and Lüders, Ber. 1933, **66** [B], 1681).

Gallium oxide is violently reduced to the metal on heating with magnesium; reduction also occurs when hydrogen is passed over the red-hot oxide although at lower temperatures the suboxide Ga_2O is apparently produced.

Gallium monoxide, GaO.—All attempts to reduce the sesquioxide result only in the formation of Ga_2O although Klemm and Schnick (Z. anorg. Chem. 1936, **226**, 353) state that the sublimate produced on heating Ga_2O_3+Ga *in vacuo* contains some monoxide. *See also* Guernsey (Physical Rev. 1934, [ii], **46**, 114) and Sen (Indian J. Physics, 1936, **10**, 429).

Gallium suboxide, Ga_2O.—Produced as a brown powder when the sesquioxide and metal are heated together at 700° and purified by subliming in a high vacuum at 500°; above 800° it begins to decompose into Ga_2O_3 and Ga. The oxide is stable in dry air and is only superficially oxidised on heating; nitric acid or bromine energetically convert it to the tervalent state; it reduces cold dilute sulphuric acid to hydrogen sulphide (Brukl and Ortner, Z. anorg. Chem. 1931, **203**, 23).

Gallium hydroxide or oxy-hydrate, $Ga(OH)_3$ or $Ga_2O_3,3H_2O$.—When a solution of a gallic salt is treated with ammonia, alkali hydroxide, carbonate or bicarbonate there is produced a white gelatinous precipitate the composition of which is somewhat doubtful and probably varies with the experimental conditions. Havestadt and Fricke (Z. anorg. Chem. 1930, **188**, 357) state that it approximates to $2Ga_2O_3,3H_2O$ while Neogi and Nandi (J. Indian Chem. Soc. 1936, **13**, 399) give

$$Ga_2O_3,3H_2O.$$

The latter authors state that on drying *in vacuo* the compound $Ga_2O_3,2H_2O$ is obtained which, unlike the freshly precipitated material, is insoluble in organic acids. A monohydrate, Ga_2O_3,H_2O, is also known and it is this compound which is obtained when the hydroxide is formed slowly or allowed to age. According to Weiser and Milligan (J. Physical Chem. 1938, **42**, 673) rapidly precipitated or un-aged samples are merely the hydrous oxide (Goldschmidt *et al.*, Norske Videnskapsakademie Arhandlinger Matem-Naturvid, Klasse, Oslo, 1925, **1**, No. 7; Böhm and Kahan, Z. anorg. Chem. 1938, **238**, 350; Laubengayer and Engle, J. Amer. Chem. Soc. 1939, **61** 1210). Gallium hydroxide is readily soluble in acids and alkalis although like aluminium hydroxide it exhibits the phenomenon of ageing. For analytical purposes it is best precipitated by boiling a slightly acid solution with sodium or ammonium sulphite or with sodium azide; tartaric and citric acids hinder precipitation. The hydroxide manifests almost equal basic and acidic properties, the latter being more pronounced than in the case of aluminium hydroxide. No metallic gallates have been produced in the wet way although compounds of the *spinel* type have been made with beryllium, magnesium and zinc, these being obtained by heating stoichiometric amounts of the intimately mixed oxides at 1,000°. Such metagallates have the general formula, MGa_2O_4, and are white crystalline compounds of which the **Mg** and **Zn** salts are rendered capable of phosphorescence by admixture with **Mg** and **Zn** metachromites.

GALLIUM AND SULPHUR.

Gallium sulphides.—The sesquisulphide, Ga_2S_3, is a yellow substance formed by heating the metal at 1,200–1,300° in a current of sulphur or purified hydrogen sulphide; it melts about 1,250° and is decomposed by water; the density is 3·48 (3·65).

Gallium monosulphide, GaS, is produced either by reducing the sesquisulphide with hydrogen or by heating the elements in the correct proportions; when sublimed at 800° it forms yellow crystals, m.p. 965°. This bivalent sulphide is stable to water, produces hydrogen sulphide with acids and burns in bromine. Heated in a high vacuum at 700° it gives a readily volatile greyish sublimate of the sub-sulphide Ga_2S, which is only slowly attacked by water. It is violently oxidised by bromine, while it decomposes when heated, producing the sesquioxide and the metal (Moser and Brukl, Monatsh. 1928, **50**, 181; 1929, **51**, 325; **52**, 253; Brukl and Ortner, *ibid.* 1930, **56**, 358; Johnson and Warren, Naturwiss. 1930, **18**, 666; Klemm and von Vogel, Z. anorg. Chem. 1934, **219**, 45).

The corresponding *selenides* and *tellurides*, with the exception of Ga_2Te, have also been made (Klemm and von Vogel, *l.c.*).

Gallium sulphates.—White octahedral crystals of $Ga_2(SO_4)_3,16H_2O$ are formed by dissolving the oxide or hydroxide in sulphuric acid and precipitating with alcohol and ether; the sulphate is insoluble in ether but is readily so in water or 60% alcohol. The dilute aqueous solution deposits a basic sulphate when heated but this redissolves on cooling. Gallium resembles aluminium in that its sulphate readily forms " alums " of the type

$$M_2SO_4{\cdot}Ga_2(SO_4)_3,24H_2O,$$

where $M{=}NH_4$, K, Rb, Cs and Tl. The solubilities of the ammonium and cæsium double salts are respectively 30·84 and 1·51 g. per 100 c.c. of solution. The ammonium "alum" behaves like gallium sulphate when dilute solutions are heated (Soret, Compt. rend. 1884, **99**, 867; 1885, **101**, 156; Tchakirian, *ibid.* 1929, **189**, 251; Dennis and Bridgman, J. Amer. Chem. Soc. 1918, **40**, 1531; Willard and Fogg, *ibid.* 1937, **59**, 1197, 2422).

Gallium selenate containing 16 and 22 mol. H_2O and a *gallium cæsium selenate* with 24 mol. H_2O are also known (Dennis and Bridgman, *l.c.*, 1558).

GALLIUM AND NITROGEN.

Gallium nitride, GaN.—When gallium interacts with ammonia at 900–1,200° there is slowly formed a dark grey nitride, GaN, of considerable stability; it is unaffected by air, water and dilute acids and dissolves only slowly in hot concentrated H_2SO_4 or $NaOH$. Hydrogen does not attack it while with oxygen above 900° it gradually forms Ga_2O_3; it may be sublimed above 800° (Johnson, Parsons and Crew, J. Physical Chem. 1932, **36**, 2651; Klemm, Jacobi and Tilk, Z. anorg. Chem. 1932, **207**, 187; Lirmann and Schdanov, Acta Physicochim. U.R.S.S. 1937, **5**, 306).

By shaking liquid gallium with active nitrogen Tiede and Knoblauch (Ber. 1935, **68** [B], 1149) obtained a nitride which differed from the above in being easily attacked by water, acids and alkalis and in losing nitrogen on heating to 150°.

Gallium nitrate.—A solution of gallium or its sesquioxide in nitric acid when concentrated and cooled deposits large, clear, hygroscopic prisms of $Ga(NO_3)_3,8H_2O$ which, according to Dupré (Compt. rend. 1878, **86**, 720), may be dehydrated in a current of warm air at 40°. At 110° it begins to decompose, conversion into the oxide being complete at 200°. If a solution of the nitrate in alcohol is treated with ether there is precipitated a white *basic salt*,

$$Ga(OH)_2NO_3,Ga(OH)_3,2H_2O,$$

and this, unlike the normal salt, is not hygroscopic (Pušin and Živadinović, Z. anorg. Chem. 1936, **228**, 255).

GALLIUM AND PHOSPHORUS.

Gallium phosphide has been obtained by passing hydrogen laden with phosphorus over the heated metal at 500°; it forms an orange-coloured mass; the corresponding *arsenide* has been made similarly.

Gallium phosphate, $GaPO_4,3H_2O$, is produced by dissolving freshly precipitated gallium hydroxide in dilute phosphoric acid and evaporating the solution; with phosphorous and hypophosphorous acids only the *acid salts*, $GaH_3(PO_3)_2,H_2O$ and $GaH_3(PO_2)_2$, are obtained. In all cases the *normal salts* may be prepared by adding to a solution of gallium nitrate one containing the sodium salt of the acid. Both *gallium phosphite* and *hypophosphite* are deposited as white precipitates of the monohydrates which are insoluble in water (Neogi and Nandi, J. Indian Chem. Soc. 1936, **13**, 399; 1937, **14**, 492).

MISCELLANEOUS COMPOUNDS.

Gallium ferrocyanide, $Ga_4[Fe(CN)_6]_3$.—Obtained as a fine, white precipitate when potassium ferrocyanide is added to a solution of a gallium salt. The precipitate is insoluble in moderately strong hydrochloric acid but dissolves in concentrated alkalis.

Gallium silicotungstate,

$$Ga_4H_{12}[Si(W_2O_7)_6]_3.$$

Readily soluble in water it forms three hydrates containing respectively 54, 81 and 87 mol. of water (Wyrouboff, Bull. Soc. Franç. Min. 1896, **19**, 342).

Gallium acetate.—A neutral acetate is unknown, the solution of gallium hydroxide in much acetic acid producing only a precipitate of the basic salt $4Ga(OAc)_3,2Ga_2O_3,5H_2O$. This loses acetic acid above 128° and at 145° there is formed $GaO(OAc)$ which passes into the oxide at 159° (Tchakirian, Compt. rend. 1929, **189**, 251; Centola, Amer. Chem. Abstr. 1936, **30**, 4386).

Neutral salts have been obtained with oxalic, tartaric, lactic, citric, malic, benzoic and anthranilic acids (Neogi and Nandi, *l.c.*; Neogi and Dutt, J. Indian Chem. Soc. 1938, **15**, 83; Levaditi *et al.*, Compt. rend. 1931, **192**, 1142; **193**, 117).

ORGANO-METALLIC DERIVATIVES OF GALLIUM.

Gallium trimethyl, $GaMe_3$.—Formed when the vapour of zinc dimethyl acts on gallium chloride, first at room temperature and then at 80–120°, the product being cooled in liquid ammonia and isolated as a white solid, m.p. −19°, b.p. 55·7°/762 mm. It is extremely sensitive to oxygen, even the solid burning spontaneously in air.

Methyl magnesium iodide reacts with an ethereal solution of gallium trichloride or bromide, yielding a trimethyl etherate,

$$Me_3Ga,Et_2O,$$

as a volatile liquid less sensitive to air than gallium trimethyl; it fumes in air and may undergo spontaneous combustion. Water and alkalis decompose it with evolution of methane (Renwanz, Ber. 1932, **65** [B], 1308). Evaporation of a solution of the etherate in liquid ammonia leaves a white residue of gallium trimethyl ammine, $GaMe_3,NH_3$, which melts at 31° and sublimes *in vacuo* at room temperature. Comparatively insensitive to oxygen it is easily attacked by alkalis liberating methane and ammonia.

Hydrogen chloride reacts with the trimethyl ammine in ether liberating gallium trimethyl which is then decomposed by the ammonium chloride also formed giving gallium dimethyl chloride monammine as a white, ether-soluble compound, m.p. 54°.

$$GaMe_3,NH_3+HCl=GaMe_3+NH_4Cl$$
$$\rightarrow GaMe_2(NH_3)Cl+CH_4$$

Further action of the acid generates gallium dimethyl chloride which is also obtainable from the trimethyl etherate. A third molecule of hydrogen chloride yields gallium methyl dichloride as a white product forming a mono- and pent-ammine; continued action of acid removes the last methyl group. If excess of hydrogen chloride be allowed to act on $GaMe_3NH_3$ at 160° there is obtained ammonium gallichloride, NH_4GaCl_4, which does not sublime *in vacuo* at 200° and which is soluble in water without apparent hydrolysis (Kraus and Toonder, Proc. Nat. Acad. Sci. 1933, **19**, 292, 298; J. Amer. Chem. Soc. 1933, **55**, 3547).

Gallium triethyl.—Viscous, unpleasant-smelling liquid formed by the interaction of gallium trichloride and mercury diethyl or lithium ethyl, m.p. −82·3°, b.p. 142·6°. Its properties resemble those of its methyl analogue; an etherate and a monammine are known, the latter being only slowly attacked by water yielding white, probably diethyl gallium hydroxide, $Et_2Ga(OH)$. From this there have been derived the corresponding chloride and sulphate (Dennis and Patnode, J. Amer. Chem. Soc. 1932, **54**, 182).

Gallium triphenyl.—Colourless, needle-like crystals, m.p. 166°, prepared by heating the metal with mercury diphenyl at 130° in nitrogen (Filman and Jones, *ibid.* 1940, **62**, 980).

Gallium acetylacetone, $Ga(C_5H_7O_2)$.—Ammonia added drop by drop, and in slight excess, to a mixture of gallium nitrate and acetylacetone first produces amorphous gallium hydroxide which soon gives place to a crystalline precipitate of the acetylacetonate. After recrystallising from acetone or benzene followed by sublimation *in vacuo* it melts at 195°; it is almost insoluble in water, cold alcohol and ether but easily dissolves in benzene, chloroform or acetone.

Gallium acetylacetone exists in three crystalline modifications (α, β and γ); the first is isomorphous with the α-acetylacetonates of Al, $Cr^{\cdots}$, $Mn^{\cdots}$ and $Co^{\cdots}$, the second or β-form with the corresponding scandium and indium compounds while γ-gallium acetylacetone is related to the iron derivative (Morgan and Drew, J.C.S. 1921, **119**, 1058; Astbury, Proc. Roy. Soc. 1926, A, **112**, 448).

G. R. D.

GALLOFLAVIN. The mordant dye galloflavin and *iso*galloflavin is obtained by the limited oxidation of gallic acid in alkaline solution; the process of oxidation depends on the amount of alkali present. Gallic acid (50 g.) is dissolved in alcohol (875 c.c.) and water (1 litre) and the solution cooled to between −5° and +5°C. Potassium hydroxide (135 c.c. of 28% solution) is then added and a current of air is passed through the mixture for 5 hours. The sparingly soluble potassium salt of galloflavin separates gradually and is collected, dissolved in warm water and precipitated with acid (Bohn and Graebe, Ber. 1887, **20**, 2327; *see also* G.P. 37934, 1886; Frdl. I, 567).

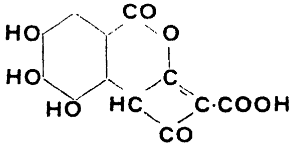
When dyed on mordanted wool, galloflavin yields with bichromate mordant an olive-yellow, with copperas a dark brown, with stannous mordant a dull orange, and with copper sulphate a brown shade. In practice, chromium mordants only are used, and the shades obtained are fast to light, milling, washing, dilute acids and alkalis. Galloflavin is used also in calico printing on a chrome mordant for greenish-yellow. The colour is somewhat sensitive to chlorine (Knetch, Rawson and Loewenthal, "Manual of Dyeing," Griffin & Co., Ltd., London, 1910, p. 623).

Galloflavin crystallises in greenish-yellow leaflets which, when heated, blacken without melting. It is sparingly soluble in water, alcohol or ether, more readily soluble in acetic acid or aniline. It dissolves in sulphuric acid forming a reddish-yellow solution which, on dilution gives a greyish-white precipitate.

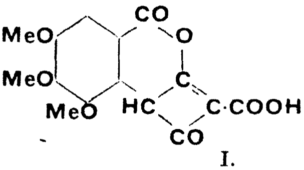
Bohn and Graebe (*l.c.*) suggested the composition $C_{13}H_6O_9$ for galloflavin and described the *potassium salt*, a yellow crystalline substance insoluble in alcohol and cold water; the *tetra-acetyl*-derivative, colourless needles, m.p. 230° (Herzig gives m.p. 230–233°); and the *tetrachloroacetyl*-compound, needles, m.p. 210–212°.

Subsequently, Herzig (Monatsh. 1910, **31**, 799) proposed the formula $C_{12}H_6O_8$ for galloflavin. On methylation, galloflavin yields the *tetramethyl ether*, colourless needles, m.p. 236–239°, and this, when quickly boiled with aqueous potassium hydroxide and then treated with concentrated hydrochloric acid, is converted into *trimethyl-isogalloflavin*, $C_{11}H_2O_3(OMe)_3{\cdot}COOH$, fine colourless needles, m.p. 253–256° with evolution of gas. The *methyl ester* of this substance crystallises from alcohol in long needles, m.p. 232–234°.

Trimethyl*iso*galloflavin contains a carboxyl group and a lactone ring; it is degraded to 3:4:5-trimethoxyphthalide by the following series of reactions, and Herzig (Annalen, 1920, **421**, 247) thus suggests for *iso*galloflavin the structure:



When distilled, trimethyl*iso*galloflavin (I) is decomposed into carbon dioxide and a substance, $C_{11}H_3O_3(OMe)_3$ (II), m.p. 130–132°, which does not react with diazomethane or acetylating agents. On warming with potassium hydroxide in aqueous methyl alcohol and then treating with hydrochloric acid, (II) is converted by fission of the lactone and four-membered rings and elimination of formic acid into the lactone, $C_{10}H_5O_3(OMe)_3$ (III), m.p. 74–77°, and this, by further treatment with alkali, yields 2:3:5-trimethyoxyphthalide (IV) and potassium acetate.



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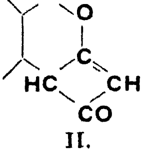

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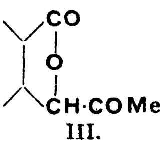

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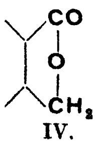
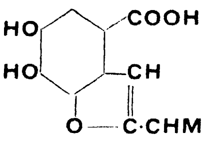
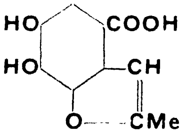


IV.

By the action of zinc dust and aqueous potassium hydroxide, *iso*galloflavin gives two acids, $C_{12}H_{10}O_7$ (V) and $C_{10}H_8O_5$ (VI), containing stable coumarone rings. The dihydroxydicarboxylic acid (V) forms silvery leaflets, m.p. 191–194° (decomp.), and is converted by methyl-alcoholic hydrogen chloride into the *methyl ester*, $C_{10}H_6O(OH)_2(COOMe)_2$, m.p. 153–156°, which yields the corresponding *diacetyl*-derivative, m.p. 71–73°. With diazomethane, (V) gives a *tetramethyl* compound, m.p. 101–103°, and this is hydrolysed to the corresponding *dimethoxydicarboxylic acid*, m.p. 200–203°.



V.



VI.

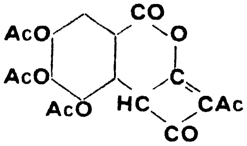
The dihydroxymonocarboxylic acid (VI), could not be obtained pure owing to the fact that it is readily oxidised in solution. With methyl sulphate it forms a *trimethyl* derivative, colourless platelets, m.p. 101–103°, which is hydrolysed to the corresponding *acid*,

$$C_9H_5O(OMe)_2COOH,$$

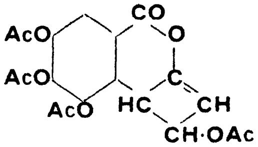
m.p. 185–188°. By treatment with methyl-alcoholic hydrogen chloride, the acid (VI) yields the *methyl ester*, m.p. 184–190° (very difficult to purify), the *diacetyl*-derivative of which melts at 109–112°.

The action of zinc dust and aqueous potassium hydroxide on galloflavin proceeds in the same manner, but the yields of the reaction products are much smaller.

With acetic anhydride and sodium acetate, *iso*galloflavin yields the normal triacetyl-compound; if zinc dust is added, however, a further acetyl-group enters, probably by displacement of the carboxyl group, giving rise to the *tetra-acetyl*-compound $C_{11}H_2O_6(COMe)_4$, (VII ?), m.p. 203–206° (decomp.) after becoming discoloured from about 180°. Similarly, trimethyl*iso*galloflavin yields *acetyltrimethyliso-galloflavin*, long, colourless needles, m.p. 138–140°. The methyl esters of trimethyl- and triacetyl-*iso*galloflavin are, however, unaffected by this treatment, and it thus appears that the presence of a free carboxyl group is an essential condition of the reaction. On the other hand, since the action only occurs in the presence of zinc dust, it is possible that the carbonyl group adjacent to the carboxyl radical is reduced, and the secondary alcoholic group is then acetylated. If such is the case, then the structure of the tetra-acetyl compound is represented by formula (VIII).



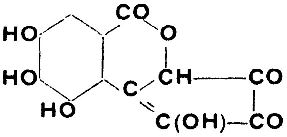
VII.



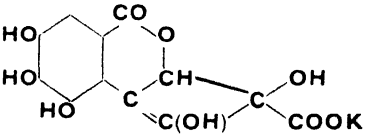
VIII.

The presence of a carboxyl group in *iso*galloflavin is proved by its conversion by methyl-alcoholic hydrogen chloride into the *methyl* ester, m.p. 300–305° after previous darkening; under similar conditions, galloflavin is unaffected.

For galloflavin Herzig suggests formula (IX) or the keto formula corresponding to this enol form. The conversion of galloflavin into *iso*galloflavin appears to proceed via the intermediate product (X) which passes, by loss of water, into *iso*galloflavin.



IX.

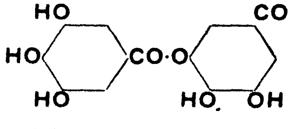


X.

A. G. P. and E. J. C.

GALLOGEN, GALLOL *v.* Gallic Acid.

GALLOTANNIC ACID, *m*-digallic acid, is obtained from tannin by repeated treatment with chloroformic ester and pyridine in an atmosphere of hydrogen (Nierenstein, Ber. 1910, **43**, 630). It crystallises from aqueous alcohol in needles, m.p. 268–270°.



GALLS. The generic term of galls includes the large variety of excrescences and other abnormal growths (cecidia, galls, cancers, hypertrophies, etc.) which are produced upon plants and animals and are caused by plant, animal and chemical irritants. The abnormal growths on plants are caused by insects, nematodes, fungi, slime moulds, bacteria and chemical and mechanical irritants. Similar growths have also been formed in plant hybrids by internal causes (Kostov, Protoplasma, 1933, **20**, 440).

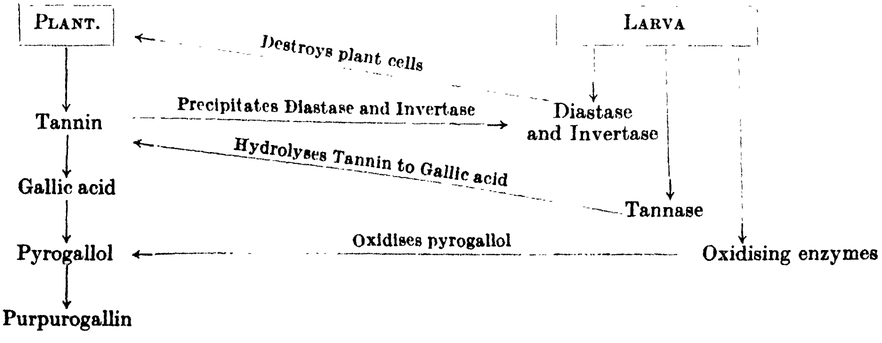
1. Plant Galls caused by Insects.

These galls were the first to attract attention and have been regarded as of great importance in all histories of drugs and of the arts of tanning and dyeing, and even to-day are among the most valued ingredients of some black inks. They are first mentioned, chiefly as medicines, in the literature of the old physicians and naturalists of Greece and Rome, the Aleppo gall and the bedeguar of the rose both being mentioned. Pliny was the first to recommend papyrus treated with gall-nuts for the detection of iron in verdigris. The first work of importance is Malpighi's "De Gallis," published in 1686, in which is advanced the theory, long since disproved, that the excitation was due to a poison secreted by the mother insect. Much literature on plant galls has since accumulated.

Source.—The insects capable of producing plant galls are principally species of *Cynips* and *Aphis*. The true oak-apple, bedeguar of the rose, the oak-gall, oak-spangles, etc., are all varieties of galls produced by insects. The nature of galls varies considerably, according to the exciting cause and the plant affected, but the official galls may be regarded as metamorphosed shoots, the metamorphosis being induced by the gall-wasp. The official drug *Galla B.P.* is the variety of gall produced by the wasp *Cynips gallæ tinctoriæ* Olivier, of which only the female is known, reproduction taking place parthenogenetically. By means of her ovipositor the wasp deposits an egg between the rudimentary leaves near the growing point of young shoots of the scrubby oaks belonging to the species *Quercus infectoria* Olivier (dyer's oak), a small tree indigenous to Asia Minor and Persia. The larva emerging from the egg wounds the delicate tissue with its mandibles and simultaneously introduces a secretion which stimulates rapid formation of tissue.

The new tissue thus developed assumes a concentric arrangement in which the larva lives, feeding on the starch produced by the cells. When mature the larva passes into the pupa stage, from which the wasp emerges and escapes by boring through the gall with its mandibles. No development of tissue takes place until a glandular secretion passes from the mandibles of the larva into the surrounding tissue which is always merismatic in nature. This formation of tissue continues as long as the exciting substance is supplied, but ceases should the larva perish. Galls should be collected preferably before the insect escapes; after this has happened they become lighter in weight and are less esteemed.

It is suggested that the inter-relationship between the gall producer and the plant is parasitic, the initial action of the larva being counteracted by tannin production on the part of the plant. The gall-larva itself produces *tannase*, which hydrolyses the tannin produced by the plant. The interaction of the tannase and also of other enzymes produced by the larva, with tannin and its decomposition products, is shown below (M. Nierenstein, Nature, 1930, **125**, 348):



Description.—The galls produced on *Quercus infectoria* Olivier, known commercially as *Aleppo* or *Turkey* galls, are nearly spherical in shape and vary from 12 to 25 mm. in diameter. The half near the stalk usually has a smooth surface, often inclined to be glossy, whereas the distal half is raised into lumps which are often conical in shape. They are hard and heavy and of a bluish-green or olive-green colour externally, yellowish or brownish-white within. There is usually a small cavity in the centre in which the remains of the larva or of the gall wasp may be found. They have no odour but an intensely astringent taste, followed by a slight sweetness. Below the epidermis is a parenchymatous tissue differentiated into three layers. The cells of the outer layer have thick walls and contain fragments of tannin; those of the middle layer have thinner walls and exhibit intercellular spaces, and also contain tannin. The cells of the inner layer have thin walls, are axially elongated and firmly adherent to one another; they contain tannin and cluster-crystals of calcium oxalate. This tissue passes into a ring of irregularly pitted, sclerenchymatous cells containing small rounded starch grains with stellate hilum. The powder is well characterised by the abundance of tannin, sclerenchymatous cells and characteristic starch grains.

Constituents.—The principal constituent of plant galls is tannic acid which, to distinguish it from other varieties of tannic acid, is termed *gallotannic acid*. A typical analysis of the Aleppo gall is given by Guibourt:

	Per cent.
Tannic acid	65
Gallic acid	2
Ellagic acid Luteo-gallic acid	2
Woody fibre	10·5
Chlorophyll and volatile oil	0·7
Brown extractive matter	2·5
Gum	2·5
Starch	2
Moisture	11·5
Sugar, albumen, K_2SO_4, potassium gallate, calcium gallate, oxalate and phosphate	1·3

The red colour of oak galls is usually ascribed to the presence of anthocyanins. Dryophantin, $C_{23}H_{28}O_{15}$, is the cause of the red colour in the red pea gall and is not allied to either the flavones or the anthocyanins, but consists of purpurogallin and 2 mol. of glucose. It sinters at 216° and has m.p. 219–220°. Incidently this is the first instance of purpurogallin found in nature (M. Nierenstein, J.C.S. 1919, **115**, 1328).

VARIETIES.—*European and Near East.*—The best galls come from Syria and are known as Aleppo galls (Turkey or Levant galls), gall nuts or galls of commerce. They are the galls formed by *Cynips gallæ tinctoriæ* Olivier on *Quercus ægilops*, *Q. infectoria*, *Q. pedunculata*, and possibly *Q. humilis*. Those gathered earliest, namely in August or September, are of the highest quality, and are at first green but subsequently become darker and harder; those gathered somewhat later, when the gall-wasp has emerged, are pale yellowish-brown, and are known as "white" galls. These are rather larger than dark galls, are lighter in weight, and are considered to contain less gallotannic acid, an opinion which is not always confirmed by analysis. Galls allowed to hang until winter become pale reddish-brown. Three qualities of Levant galls may be distinguished: (i) Aleppo galls, small (2·5 cm. diameter), dark green to black in colour; (ii) lighter-coloured galls presenting the appearance of having been powdered on the surface; (iii) Smyrna galls, larger (3–5 cm. diameter), usually yellowish in tint. The dark-hued galls sink in water whereas the inferior lighter tinted galls (even when dyed to imitate the former) float.

Galls of a similar type are obtained in Southern Europe from the scrubby oaks (*Quercus sessiliflora* and *Q. pubescens*. English galls are smooth and globular and, having been gathered late, after the emergence of the gall-wasp, are usually pale brown in colour and perforated by the exit-hole gnawed by the insect. They are much less active than the Aleppo galls, containing only 15–20% gallotannic acid. The galls of *Cynips kollari* Hartig, the so-called marble galls or oak-apples, are produced on several species of *Quercus* in Southern Europe, North Africa and Asia Minor, and the gall-wasp also occurs in England where it is widely distributed. The galls of *Cynips calicis* Burgsdorff, known in Germany as Knoppern, are formed on *Quercus ægilops*, *Q. pedunculata*, and occasionally on *Q. pubescens* and *Q. sessiliflora*. They are 15–20 mm. long and 18–25 mm. broad, dark brown to black in colour and almost woody. They occur in Austria, Hungary, Slavonia, Serbia, Greece and Asia Minor. Their maximum yield of tannin is 50%.

The bedeguar, or mossy rose gall, is produced by *Rhodites rosæ* Linnæus on several species of the genus *Rosa*. It occurs naturally in Europe and West Africa and has been introduced into America.

American galls.—Galls found on *Quercus virens* closely resemble the Aleppo gall, containing 40% tannin (Trimble, Amer. J. Pharm. 1890, **72**, 563). Their maker has been identified by S. A. Rohwer as *Disholcaspis cinerosa*. The gall occurring in America on *Rhus glabra* differs from all those mentioned above, and is similar to the Chinese gall mentioned below, in being produced by an aphid instead of a gall-wasp. The insect concerned in its formation is identified as *Melaphis rhois* Fitch.

Japanese and Chinese galls are produced by *Aphis sinensis* Bell on *Rhus semialata*. They are of a very irregularly lobed shape, reddish-brown in colour, and covered with a thick grey velvety down. They are largely used in the manufacture of gallotannic acid of which they contain about 70%.

II. Plant Galls caused by Bacteria.

Galls caused by bacteria show considerable variation and may be divided into three groups:

(*a*) Those in which the bacteria occupy small pockets and stimulate the surrounding cells, *e.g.* Olive root.

(*b*) Those in which the bacteria are within the cells, *e.g.* bacteria forming legume nodules.

(*c*) Those of the crown-gall type.

A marked difference between some of the bacterial galls and galls due to other causes is the presence of tumor strands in the crown gall. *Crown-galls* have received much attention in recent years because they show a cytological similarity to animal and human cancer. This is especially true of galls formed by *Bacterium tumefaciens* and *Phytomonas tumefaciens*. Tumors produced by *B. tumefaciens* have been found to be similar in structure to those formed by injection of various chemicals into the internodal cavities of Ricinus. The action of chemicals in producing tumors is paralleled by their ability to cause precipitation in tissue experiments (Kostov and Kendall, Arch. Mikrobiol. 1933, **4**, 487). Vitamin C has been shown to increase the size of tumors produced on tomato plants by *P. tumefaciens* (Havas, Amer. Chem. Abstr. 1936, **30**, 1850). Growth substances obtained from *P. tumefaciens* produce effects similar to those of heteroauxin in the bean hypocotyl. These growth substances give the characteristic test of β-indolylacetic acid indicating that this substance, or a closely related indole compound, is the heteroauxone produced by *Phytomonas tumefaciens* (Link and Wilcox, Science, 1937, **86**, 126). Plant tumors contain a higher organic nitrogen content than the healthy tissues. Pathogenic and nonpathogenic sister-cell cultures of the crown gall of tomatoes grown above and below the critical temperature showed no significant differences as regards reduction of nitrates, fermentation of sugars and related substances, CO_2 production, cataphoretic velocity, osmotic pressure and oxidation–reduction potential induced. The gall tissue showed more ash, alkalinity, total N, oxidising enzymes and respiratory activity but less cellulose, starch, pentoses and reducing sugars than the contiguous healthy tissue (Riker, Rept. 3rd Intern. Congr. Comp. Path. 1936, **1**, **2**, 107).

III. Plant Galls caused by Fungi.

Fungi are the causes of many abnormal growths such as cedar apples, peridermial growths on conifers, witches' brooms and other hyperplasias of various types. The most common cases are the cedar-apple rust fungi. Their structures have received little attention.

Slime moulds are the causes of some abnormal growths. For example, the " club root "disease of cruciferous plants caused by *Plasmodiophora brassicæ*.

IV. Plant Galls caused by Chemical Substances.

After successfully producing abnormalities by the use of a number of chemical substances, Smith in 1917 came to the conclusion that any soluble substance whatever, except a killing, a plasmolytic or an oxygen-absorbing substance, if continually liberated locally in excess in tissues would be competent to induce tumor formation. Recently many experiments have been carried out with such compounds as β-indolylacetic acid, β-indolylpropionic acid, α-napthylacetic acid, etc., for comparison with the galls produced by an extraction of *P. tumefaciens* and other bacteria (Brown and Gardner, Phytopath. 1936, **26**, 708; 1937, **27**, 1110; Solacolu and Constantinesco, Compt. rend. 1937, **204**, 290; 1938, **206**, 1985).

GALUTOLIN. A flavone glycoside, which on hydrolysis yields glucose and luteolin (5:7:3′:4′-tetrahydroxyflavone).

GALVANISED IRON. Iron coated with a protective layer of zinc. The layer is deposited by (*a*) electrogalvanising, (*b*) dry galvanising, or (*c*) galvanising with molten zinc. The last is the most widely applied process and is used for the protection of wire, wire netting, corrugated iron and other forms of sheet iron.

(*a*) Electrogalvanising (*v*. Vol. IV, 267*d*).

(*b*) " *Sherardizing* " consists in heating the articles to be plated in closed boxes and covered with zinc dust containing about 10% oxide and 3% carbon. The temperature is kept below the fusion point of zinc and the vapour slowly deposits a dull coating which, however, wears satisfactorily (Cowper-Coles, B.P. 9927, 1901).

(*c*) In the true galvanising process the iron is first pickled in 12–20% hydrochloric acid and scale removed by washing with water and, if necessary, sand. It is then immersed in molten zinc covered with ammonium chloride which acts as a flux. On emerging from the zinc bath the sheet metal is usually treated with rolls or wire brushes to improve the surface. In work of better quality tin is added to the molten metal, often in the form of lead solder, to impart a pleasing spangle to the finished surface.

" GALVENE " (*v*. Vol. III, 77*a*).

GAMBIER (*v*. Vol. II, 433*b*).

GAMBOGE. This gum resin, more properly, but never, termed Camboge, is the product of *Garcinia Hanburyi* Hook *F*. (Fam. Guttiferæ), a tree found in Siam, Cambodia and the southern part of Cochin China. Bamboo stems are attached to incisions in the trees, and the milky exudation thus collected dries and yields the gum-resin in the familiar pipe form. It is used to a small extent in medicine as a purgative and also to lower blood pressure in cases of cerebral congestion. It has a fine yellow to orange colour and is the basis of many yellow water-colour pigments; it was known to the Chinese as early as the 13th century.

Gamboge contains from 70 to 80% of resin, 15 to 25% of gum and small amounts of organic debris. The commercial article has the following characters:

Acid value	65–90
Ester value	45–65
Saponification value . . .	125–145
Ash	Under 1%
Moisture	3–5%

The resin, extracted by alcohol, should have an acid value 85–105, ester value 55–75 and saponification value 150–175.

E. J. P.

GAMBUFOGENIN (*v*. Vol. II, 388*b*).

GAMBUFOTOXIN (*v*. Vol. II, 388*b*).

" GANDKAKI " (*v*. Vol. I, 499*a*).

GANISTER. A local name of unknown origin for a hard siliceous sandstone occurring in the Coal-measures of the north of England. Formerly it was employed as a road-stone, but now is much used for making refractory ganister- or silica-bricks and for the linings of steel furnaces and converters. The name has been also loosely applied to other siliceous materials used for making fire-bricks. In the typical locality, namely in the neighbourhood of Sheffield, the rock occurs beneath thin seams of coal at a definite horizon—the Ganister group—in the lower Coal-measures. The best bed, lying immediately beneath the Hard Mine coal, varies in thickness from a few inches to 5½ ft., with an average of 2½ ft. Here it is a hard compact rock with a very fine and even-grained texture, and consists of sub-angular grains of quartz, mostly 0·15–0·5 mm. across, closely packed together and cemented with secondary silica. No appreciable amounts of mica, felspar or carbonates are present. The rock thus has the character of a quartzite. It is light to dark grey in colour, and is often iron-stained along the joint surfaces. It breaks with a splintery to sub-conchoidal fracture with sharp edges. Carbonaceous patches and streaks and fossil tree-roots are embedded in the rock. It consists of 90–95% of silica with small amounts of alumina, iron oxides, lime and alkalis. Sp.gr. 2·59. Silica rocks of very much the same nature are widely distributed in most of the coal-fields of England, Wales and Scotland; *e.g.* the Dinas rock (or " clay ") from the Vale of Neath in Glamorganshire, which contains as much as 98% of silica. They pass insensibly, both laterally and vertically, into siliceous fire-clays ("bastard ganister"). The rock is won by quarrying or underground mining, and is crushed, ground and mixed with lime (1–1½%) or fire-clay to act as a binder. This mixture is moulded into bricks, which, after drying, are fired at about 1500°, or it is applied directly as a furnace lining, or used for setting the bricks and patching and repairing furnaces. Ganister is also ground to a fine sand for use in casting iron and brass. (*See* Mineral Resources of Great Britain, Mem. Geol. Survey, 1918, **6** (2nd ed., 1920); and 1920, **16**; A. B. Searle, "Refractory Materials," 3rd ed., London, 1940.)

L. J. S.

"GARANCINE" (*v.* Vol. II, 524*d*).

GARBAGE FATS. Under the name "garbage fats," or "garbage grease" may be comprised all the fats recovered from household and similar domestic refuse. (In the United States, hotel and restaurant wastes are usually disposed of separately and worked up for "house grease" or "kitchen grease.") Such refuse is generally collected by the municipal authorities and disposed of as soon as possible by consuming it in specially designed destructors. The method is simple, although theoretically wasteful, since the fat and other possible feeding materials are destroyed with all the putrescible matter.

The utilisation of domestic and hotel food-refuse as pig-feed has been practised as a war-time measure in many European countries: it was adopted for a time as a regular means for the large-scale disposal of garbage by certain American cities, but was abandoned on account of the difficulties involved in the collection and transport of the fresh garbage, and also because the quality of the pork and lard obtained from hogs so fed was not suitable for the requirements of the American packing industry.

However, efforts have not been lacking to recover the considerable fat content of garbage, and in the United States especially, methods for the rational disposal of this material have been developed.

An early process (worked in Buffalo about 1885) consisted in extracting the garbage with petroleum spirit, and a solvent plant was still in use in Chicago in 1929, although Zapoleon writes that "the city of Chicago is about to abandon (municipal) reduction and turn to incineration" (Zapoleon, "Inedible Animal Fats in the United States," Fats and Oils Studies, Stanford Univ., No. 3, 1929).

Solvent extraction, however, has largely been superseded by cheaper processes, comprised under the term "reduction processes," which are similar to the methods used in the rendering of bone grease, slaughterhouse greases and inedible fats generally, and consist in boiling the garbage with steam under moderate pressure. After the boiling, the mass is allowed to settle, and the grease in the top layer is collected. (The Indianapolis system of garbage collection and steam-rendering is described in detail by Zapoleon, *op. cit.* pp. 224–226). The grease is sold for the manufacture of low-class soaps and lubricants. It has a dark brown colour, and is characterised by the presence of a large amount of free fatty acids and unsaponifiable matter. Not infrequently it develops an unpleasant odour when kept.

Data collected by Zapoleon show that the eighteen large cities in the United States which operated reduction plant processed rather more than a million tons of raw "green" garbage in the year 1928, the total production of garbage grease being estimated at about 22,300 tons.

E. L.

GARDENIA GRANDIFLORA. The fruit of the *Gardenia grandiflora* L., known as "Wongsky," is or was employed in China for dyeing yellow, as an assistant for the production of green colours, and in conjunction with safflower.

Rochleder and Mayer (J. pr. Chem. 1858, [i], **74**, 1) isolated from it pectin, the rubichloric acid (chlorogenin) which is present in madder (Rochleder, Annalen, 1851, **80**, 321), tannin and a red amorphous colouring matter apparently identical with the crocin of saffron (*Crocus sativus*). By hydrolysing the colouring matter, Kuhn, Winterstein and Wiegand (Helv. Chim. Acta, 1928, **11**, 716) obtained crocetin, identical with the product isolated from saffron.

Bancroft, "Philosophy of Permanent Colours," London, 1813, p. 285, mentions the use of the *Gardenia florida* L. by the Chinese for the dyeing of scarlet under the name of "unki." From the fruit of this plant, which some botanists believe to be the same as, or at least very similar to, *G. grandiflora*, Munesada (J. Pharm. Soc. Japan, 1922, No. **486**, 666) isolated the colouring matter by extraction with water. Hydrolysis with acid yielded an amorphous powder which was shown to be identical with crocetin.

The *Decamalee* or *Dekamali* gum, which is obtained in India from the *Gardenia lucida*, contains, according to Stenhouse and Groves (Annalen, 1880, **200**, 311), *gardenin*, $C_{14}H_{12}O_6$, deep yellow crystals, m.p. 163–164°, insoluble in water and alkaline solutions. Addition of nitric acid to a hot solution of the colouring matter in acetic acid yields *gardenic acid*, $C_{14}H_{10}O_6$, deep crimson needles, m.p. *c.* 223° (decomp.), the *diacetyl*-derivative of which forms bright orange-red needles darkening at 230° and melting at about 224°. Gardenic acid is converted by means of sulphurous acid into *hydrogardenic acid*, $C_{14}H_{14}O_6$, lustrous needles, m.p. 190°.

It is improbable that gardenic acid is a carboxylic acid, as was at first assumed; its behaviour with reducing agents and with alkaline solutions points rather to a quinone grouping.

A. G. P. and E. J. C.

GARCININ (this Vol., p. 380*a*).

GARCINOL (this Vol., p. 380*b*, *c*).

"GARDENAL" (*v.* Vol. I, 623*a*).

GARDENIC ACID *v.* GARDENIA GRANDIFLORA.

GARDENIN *v.* GARDENIA GRANDIFLORA.

GARDENIOL. The perfume known as gardeniol is phenylmethylcarbinyl acetate,

$$\text{PhMeCH·OAc}.$$

It occurs naturally in gardenia oil, and is prepared artificially and used in fine floral perfumes.

Phenylmethylcarbinol is also known as α-phenylethylalcohol.

The alcohol has the following characters: m.p. 20·9°; b.p. 204–207°; sp.gr. 1·018 at 15·5°; rotation ±0°; ref. ind. 1·5273 at 20°. The acetate has b.p. 218°; sp.gr. 1·069 at 15·5°; and ref. ind. 1·5048 at 20°.

E. J. P.

GARLIC.—*Allium sativum.* A plant grown largely in Mediterranean countries. The onion-like bulb forms the well-known condiment. *A. scorodoprasum* (or *rocamboll*), a related species, grows wild in certain parts of Europe and also in the east. *A. vineale*, a smaller wild species, often occurs in pastures and if eaten by cows may contribute its characteristic odour to milk. König records the analysis of *A. sativum* bulb as: water 64·6, protein 6·8, fat 0·1, carbohydrates 26·3, fibre 0·8 and ash 1·4%. A later analysis (Agcaoili, Philippine J. Sci. 1916, **11**, 91) showed water 88, protein 2·2, fat 0·32, N-free extractives 7·27, fibre 1·17 and ash 1·03%. The odoriferous principle of garlic is an essential oil (approx. 0·2%) which according to Semmler (Arch. Pharm. 1892, **230**, 434) consists of allyl disulphide 60%, a trisulphide

$$C_3H_5{\cdot}S{\cdot}S{\cdot}S{\cdot}C_3H_5$$

20% with smaller proportions of allyl propyl disulphide. Other workers record the presence of allyl *iso*thiocyanate. Braecke (Mem. Acad. roy. Belge, classe sci. 1921, [ii], **6**, No. 6, 1) has isolated a sulphur-containing glycoside, hydrolysed enzymically to fructose and a volatile oil. K. Daigo (J. Chosen Med. Assoc. 1935, **25**, 439) in an examination of *A. scorodoprasum* also reports the occurrence of a glucoside *alliumin* yielding glucose and magnesium allyl sulphide and attributes the odour of the bulbs to an essential oil derived from the breakdown of the glucoside. Chevastelon (J. Pharm. Chim. 1895, [vi], **2**, 83) obtained inulin from garlic bulbs, it showed a specific rotation of −39°, was hydrolysed by acid and by mutase (from *Aspergillus niger*) to lævulose, but was unacted upon by yeasts or amylase. A fructan *scorodose*, hydrolysed largely to lævulose, has been isolated from *A. scorodoprasum* by Y. Kihara (J. Agric. Chem. Soc. Japan, 1935, **11**, 548).

A. G. Po.

GARLIC, ESSENTIAL OIL OF *v.* GARLIC.

GARNET (Ger. *Granat*; Fr. *Grenat*). A group of minerals differing widely in chemical composition, but all conforming to the general orthosilicate formula $R_3''R_2'''(SiO_4)_3$, where R''=Ca, Fe, Mg, Mn; and R'''=Al, Fe, Cr, or rarely Ti. The following principal types may be distinguished:

Calcium-iron-garnet	$Ca_3Fe_2Si_3O_{12}$ Andradite
Calcium-chromium-garnet	$Ca_3Cr_2Si_3O_{12}$ Uvarovite
Calcium-aluminium-garnet	$Ca_3Al_2Si_3O_{12}$ Grossular
Iron-aluminium-garnet	$Fe_3Al_2Si_3O_{12}$ Almandine
Magnesium-aluminium-garnet	$Mg_3Al_2Si_3O_{12}$ Pyrope
Manganese-aluminium-garnet	$Mn_3Al_2Si_3O_{12}$ Spessartine

Only exceptionally is the composition of actual garnet crystals as represented above. As a rule, several, or even all, of these compounds enter into isomorphous mixtures; and whilst there is generally a preponderance of one or other of them, this is not always the case. All the members of the group crystallise in the cubic system, usually with the form of the rhombic dodecahedron or the icositetrahedron, or a combination of these. The crystals are often rounded or granular in form. There is no cleavage, and the lustre often inclines to resinous in character. Corresponding with the wide range in chemical composition, these minerals exhibit a wide range in colour (yellow, brown, red, green, black, rarely colourless, but not blue), transparency, sp.gr. (3·15–4·3), hardness (6½–7½), and mode of occurrence. They occur as primary constituents of igneous rocks; in gneisses, schists and crystalline limestones; in veins and encrusting the walls of crevices in rocks. Granular rocks composed wholly of garnet are also known.

The chief application of garnet is as a gem-stone, of which there are several beautiful varieties. *Hessonite*, or cinnamon-stone, is a variety of calcium-aluminium-garnet, containing small amounts of ferrous and manganous oxides; its colour is a warm yellowish-red. *Almandine* is deep red, often with a violet tinge. *Pyrope* (Bohemian garnet, "Cape ruby") is a fiery red. *Rhodolite*, a variety midway between almandine and pyrope in composition, is remarkable for its delicate rhododendron-red colour. *Demantoid* is a calcium-iron-garnet of a rich emerald-green colour and with a brilliant lustre and a dispersion of the refractive indices even higher than in diamond.

Garnet is also used as an abrasive agent, mainly in the form of sand, for sawing and grinding stone and for making garnet-paper (often sold as "emery-paper"). Owing, however, to its lower degree of hardness, it is of less value than corundum and emery. Practically the whole of the massive garnet used for this purpose is mined in the eastern United States, principally New York, but also Connecticut, Pennsylvania and North Carolina. The output amounts to about 5000 tons per annum, valued at about £6 per ton. In the garnet-mining district of the Mittelgebirge in northern Bohemia, the small material, left after picking out the stones suitable for cutting as gems, is used for gravelling garden walks.

L. J. S.

GARNIERITE. A hydrated silicate of magnesium and nickel, of importance as an ore of nickel. It is soft and earthy, greasy to the touch, and usually of a bright apple-green colour; sp.gr. 2·3–2·8. The composition is variable (SiO_2 35–52, MgO 2–37, NiO 2–50, H_2O 10–20%), and the material is probably a mixture. It may be regarded as a hydrated magnesium silicate, allied to serpentine, in which variable proportions of magnesium are replaced by nickel. The darker green varieties are sometimes distinguished by the name *noumeite* (from Noumea in New Caledonia), the name garnierite (after Jules Garnier, the discoverer of the New Caledonian nickel ores) being reserved for the lighter-coloured varieties. A chocolate-coloured variety, containing iron, has been called *chocolite* (J. Garland, Nickel Mining in New Caledonia, Trans. Inst. Mining and Metall. 1894, **2**, 128, 224). *Nepouite*, from Nepoui, New Caledonia (E. Glasser, Compt. rend. 1906, **143**, 1173), is a finely crystalline variety for which the formula is given as $3(Ni,Mg)O.2SiO_2.2H_2O$, the amount of nickel oxide ranging from 18 to 50%.

These minerals occur in veins traversing serpentine rocks in the neighbourhood of Noumea, or Numea, the capital of New Caledonia; and, like the serpentine, they have been produced by the alteration of peridotite rocks, the olivine of which contains traces of nickel. Over 100,000 tons of these nickel ores are exported annually from New Caledonia.

Large deposits, forming beds 10 metres in thickness, of the same type of ores occur, also in connection with serpentines and olivine rocks, at Riddles, in Douglas Co., Oregon. The nickel mineral from this locality is sometimes referred to *genthite*, $2NiO.2MgO.3SiO_2.6H_2O$. Other similar occurrences are met with and to some extent mined at Webster in North Carolina, at Texas in Lancaster Co., Pennsylvania (genthite), at Revda in the Urals (*revdanskite*), and near Frankenstein in Prussian Silesia (*pimelite*, *alipite*, etc.).

On the New Caledonian ores, *see* A. Liversidge, "The Minerals of New South Wales," etc. 1888, 275; F. D. Power, Trans. Inst. Min. Met. 1900, **8**, 426, with bibliography; E. Glasser, Ann. Mines, Paris, 1903, [x], **4**, 363.

L. J. S.

GAS, AIR. Air-gas or carburetted air is made by charging air with the vapour of a liquid hydrocarbon. The possibility of employing air-gas for heating and lighting purposes was realised early in the nineteenth century. The difficulties and drawbacks which were associated with its use, and which hindered its development, did not disappear until technological advances had been made in other fields. The most important of these developments were the invention of the incandescent mantle and the availability of low-boiling hydrocarbons consequent upon the development of the American petroleum industry.

Air-gas is generally manufactured where coal-gas is not available and with the general growth in gas and electricity services has come a lessened need for it. Furthermore, in its own sphere of application it has now to compete with "bottled gas" obtained from natural sources or by petroleum cracking, and with electricity made by petrol-driven generators. Consequently air-gas is to-day but little used.

An air-gas plant comprises a generator, a gas holder with the necessary distributing pipes and burners.

At the generator, an air stream is produced by a pump or fan, suitably driven by a falling-weight or by a gas-engine. The air then passes into a carburetting chamber where it is charged with petrol vapour, mechanical means being employed to maintain a constant percentage of hydrocarbon in the issuing gas, and at a value outside the lower and upper explosion limits of 8 and 12%, respectively (H. F. Coward and G. W. Jones U.S. Bur. Mines, Bull. 279, revised ed. 1939).

In one form of apparatus, a pump working on the principle of the rotary wet gas-meter delivers a steady stream of air. The air passes through a tortuous tube, countercurrent to a stream of petrol, which is supplied at a constant rate by a drip-feed.

For descriptions and references concerning a wide variety of generators, *see* Engler and Höfer, "Das Erdöl," Vol. IV, pp. 494–499 (1916).

The gas issuing from the carburettor then passes to a holder and thence to burners of the Bunsen type. Safety devices, such as gauze-packed tubes, are usually inserted between the gas holder and burners, in order to prevent the possible spread of an explosion wave.

The quality of air-gas is dependent both on the nature and on the quantity of hydrocarbons it contains. With regard to quantity, mixtures passing the upper explosion limit are usually employed in preference to those falling below the lower limit, on account of their higher calorific value and higher flame temperature. They are at a disadvantage, however, with respect to their high dew-point, which render them very prone to condensation during cold weather.

An aviation petrol is usually used as the carburetting liquid. However, the use of a volatile petroleum-cut boiling over a narrow range, *e.g.* from 30 to 40°C., is advantageous in that the composition of the gas suffers less change as the bulk of the petrol evaporates.

Tulpov (J. Appl. Chem. Russia, 1929, **2**, 395), employing an aviation petrol, sp.gr. 0·720, found that the various constituents evaporated in proportion to their partial vapour-pressures in the mixture. The following data were obtained with a gas prepared at 10–20°C.: hydrocarbon content 99–193 g./m.^{3}, *i.e.* 12·3–18·5% by volume; calorific value 1,020–2,000 kg.-cal./m.^{3}, flame temperature 675–1,318°C. He concluded that this gas was suitable for use at temperatures not below 15°C.

F. H.

GAS ANALYSIS (*v.* Vol. II, 674).

GAS BLACK (*v.* Vol. II, 312*b*).

GAS BLUE (*v.* Vol. III, 473*b*).

GAS, COAL. During the 17th and 18th centuries the evolution of a combustible gas which burnt with a luminous flame was observed in the neighbourhood of coal-fields. It was also observed that a gas of this nature could be produced by the distillation of coal in a closed vessel. The first to carry out the process of the distillation of coal for the special purpose of producing a gas for use as an illuminant was William Murdoch, who in 1792 lighted his house at Redruth by this means. At that time Murdoch was in charge of James Watt's condensing steam engines, then recently erected at Cornish mines by Messrs. Boulton and Watt, of which firm he was the representative. On returning later to the works of Messrs. Boulton and Watt he continued his investigations on the production of coal gas and by about 1798 had developed his process sufficiently to light part of the works. Independently of Murdoch, but at a rather later date, Phillipe Lebon of Paris employed for lighting purposes the gas evolved by the distillation of wood, the date of his first patent being 1799. At peace celebrations in this country in 1802 a public display of the new gas lighting was given. This was followed by the installation of gas-lighting plant in a number of factories and large houses.

In 1806 F. A. Winsor, a Moravian, arrived in this country. He came with an ambitious scheme, originated by Lebon, for the erection of a gasworks for a public supply of gas. His proposals "to provide streets, squares and houses with gaseous lights by means of conducting tubes underground from distant furnaces, on the principles as houses are now supplied with water," met with considerable opposition from the timid and the superstitious and also from vested interests. It is probable that the extravagant claims made, notably regarding financial returns, adversely affected his case. In spite of opposition, Winsor lighted the street of Pall Mall, London with gas in 1807 as an earnest of his intentions. At the inquiry which followed, Winsor and his witnesses commended the safety and cheapness of gas for lighting, the value of coke as a smokeless fuel and the usefulness of tar and ammonia.

Winsor received considerable assistance from Fredrick Accum, a chemist whose investigations had already made him well known in London. Prior to Winsor's first patent in 1804, Accum had already interested himself in the chemistry of gas production and, at the request of the promoters of the new company, conducted an extensive series of experiments. In his testimony before the Committee of the House of Commons appointed in 1809 to consider the application for a charter, Accum described his experiments in the utilisation of the by-products of gas manufacture. These experiments are important for they represent the first efforts for the utilisation of these important by-products. Parliament eventually passed a bill which permitted the incorporation of Winsor's Company in 1810, and the Chartered Gas Light and Coke Company was established in 1812, with Accum on the first board of directors as practical chemist. This company still continues under the name of the Gas Light and Coke Company.

Other companies followed that of Winsor, and in a comparatively few years the manufacture of gas became general practice. In 1847 Parliament controlled the powers of gas companies and prohibited the production of gas of inferior quality, and in 1860 areas of supply were allocated to each undertaking. From that date the gas industry has steadily increased.

The almost exclusive use for coal gas until the last quarter of the 19th century was for lighting purposes, by utilising the luminosity developed by burning it, the illuminating power being a quality of the first importance. The method formerly employed consisted in burning the gas in open flame burners. The introduction of the incandescent mantle by Auer von Welsbach in 1887 revolutionised gas lighting. This method of lighting, in which a mantle composed of thoria and ceria is heated to incandescence by a Bunsen flame, has replaced the old "batswing" burner which is now obsolete. With the incandescent burner, the light evolved is dependent mainly on the calorific power of the gas, but has no direct connection with its illuminating power when burnt in open flames. Moreover, during the last 50 years, a steady increase in the employment of gas for the purposes of heating and cooking, as well as for the production of power in gas engines, has also emphasised the fact that the calorific power of the gas is of primary importance so far as the great bulk of the gas supplied is concerned.

Until about 1880 gas undertakings were subjected to little effective competition, but from that time competition has steadily increased, on the one hand from electricity and on the other from the introduction of cheap mineral burning oils. The stimulus of effective competition has resulted in a much more rapid advance, both in the technical aspects of the manufacture of the gas and in the commercial methods adopted for its sale.

It will be understood that gases derived from sources other than the carbonisation of coal (*e.g.* blast-furnace gas, refinery and natural petroleum gases, etc.) can be used in certain circumstances for purposes similar to those for which coal gas is employed. In this section, however, only the production of what is ordinarily known as coal gas will be considered, that is the gas distributed from the gasworks for public use and capable of being employed at the desire of the consumer for lighting, heating or power purposes. The magnitude and extent of this industry and the manner in which it has extended during 50 years is shown in Table I, giving the summary of the figures in the Board of Trade returns for

TABLE I.—GROWTH OF THE GAS INDUSTRY.

(Figures relate to authorised undertakings.)

Year.	Capital employed. £.	Length of gas mains. Miles.	Number of consumers.	Coal carbonised. Tons.	Coal gas made. 1,000 cu. ft.	Water gas made. 1,000 cu. ft.	Coke oven gas purchased. 1,000 cu. ft.	Total gas sold. 1,000 cu. ft.[2]
[1]1885	55,132,986	18,967	2,095,025	8,378,904	84,637,728	—	—	77,393,670
[1]1905	124,194,221	30,931	5,064,075	14,480,325	155,167,831	19,736,859	—	161,407,725
[1]1913	139,727,277	39,099	7,103,113	16,971,724	195,826,569	23,778,609	—	206,474,478
[1]1920	158,266,091	40,332	7,635,222	17,944,377	219,718,988	38,225,179	—	241,018,701
1927	183,405,321	45,821	8,686,339	17,703,593	246,113,651	47,130,358	5,340,223	280,201,562
1935	220,656,515	59,010	10,516,759	17,293,900	260,505,328	32,354,744	20,454,577	295,856,918
1936	225,849,568	61,593	10,775,444	18,334,048	274,949,811	27,458,821	24,329,216	309,935,818
1937	233,149,039	63,436	11,009,745	18,650,122	279,453,806	27,359,581	28,028,000	316,400,000

[1] Includes Ireland.

[2] Includes relatively small quantities of Mond gas, producer gas, etc.

all authorised gas undertakings belonging to 700–800 statutory gas companies or local authorities for the years 1885–1937.

This table does not include the production of private companies, but their combined output is relatively very small and would not materially affect the figures. The total amount of coal carbonised by these small private undertakings is only about 700,000 tons annually, *i.e.* less than 4% of the total.

In addition to the gas output, coke, tar and ammonia are also produced in large quantities as by-products. The amounts produced by authorised undertakings in 1936 were as follows: 12,286,000 tons of coke and breeze, 233,656,000 gallons of tar and 86,345 tons of sulphate of ammonia (Board of Trade Return).

So far as the actual carbonisation of the coal is concerned, Murdoch, after experimenting with different types of retort, settled down to the employment of long narrow retorts set horizontally. The coal was charged into these all at once, a free space being left above the charge throughout the whole length of the retort. The charge was then allowed to remain in the retort until completely carbonised, when the residual coke was raked out and the retort recharged with more coal. At first cast-iron retorts were employed, but the rapid wearing of these, especially when the temperature of carbonisation was increased, soon led to the substitution of fireclay for cast iron.

After the coal-gas industry became firmly established there was for a long time no material alteration in the principles of manufacture evolved by Murdoch and his immediate successors, prominent among the latter being Samuel Clegg and his son, Samuel Clegg, junr. At the same time very considerable changes took place in the details of the plant and in the construction of apparatus of larger size, coincident with a constantly increasing demand for gas.

The carbonisation of the coal and the treatment of the hot volatile products issuing from the retorts to obtain a gas suitable for distribution still, broadly speaking, follows the lines adopted in the earlier days of the industry. These products are first cooled to approximately atmospheric temperature, when considerable vapours liquefy, forming tar, and the steam present in quantity condenses to water. This water dissolves part of the ammonia which is present in the crude gas as well as other gaseous impurities, notably hydrogen sulphide and carbon dioxide. The remainder of the ammonia is removed by washing with water. For the further purification of the gas after ammonia removal, it must be subjected to a process for the elimination of hydrogen sulphide. This was effected in the earliest stages of the industry by treatment with milk of lime. This was later replaced by moistened slaked lime, placed in layers in a closed purifier, constructed in such a manner that the gas filtered through successive layers of this material. Still later, slaked lime was replaced by hydrated ferric oxide placed in similar purifiers. This last substance, unlike the slaked lime, does not simultaneously remove the remainder of the carbon dioxide present in the gas. It was either separately removed by lime or allowed to remain. Early researches on ammonia recovery and gas purification are associated with the name of Richard Laming, whose activities are reflected in the patent literature of the period 1841–64.

The technical advances, until comparatively recent times, involved no great alterations in principle. They consisted generally in improving the efficiency and economical working of the plant employed, and in the introduction of mechanical transport for the large quantities of material to be dealt with, including the adoption of labour-saving machinery. Further, the temperatures at which the coal is carbonised have been increased, resulting in a larger yield of gas per ton of coal.

The present century has witnessed considerable advances in the technique and efficiency of gas manufacture. These advances have been coincident with the extensive development of gas as a heating medium for both domestic and industrial purposes. There have been striking reductions in the cost of gas manufacture, due to the adoption of scientific control of the works, coupled with more efficient methods. The purity of the gas sold and the thermal efficiency of its utilisation have also improved. Standards of gas purity are prescribed by Parliament, but the gas industry has gone far beyond these standards and has introduced additional refinements, such as the removal of naphthalene and moisture. In addition, progress is being made in the removal of organic sulphur compounds and recent research suggests the probability of further important advances in this direction.

From the point of view of conserving national fuel, the efficiency of the carbonisation process as measured by the heat value of the products sold from a gasworks varies from 75 to 87% of the heat energy of the coal treated. The attainment of this efficiency is reflected in the figures shown in Table II below. In this the average quantity of gas produced each year, per ton of coal, by authorised undertakings, has been calculated from the Annual Returns of the Board of Trade. It will be seen that a halt has been reached in the ratio of gas to coal. It should not be assumed from this, however, that finality in carbonisation development has been reached.

TABLE II.

Year.	Gas per ton of coal, cu. ft.
1919	12,100
1924	13,380
1929	14,245
1934	15,004
1937	14,984

The net thermo-chemical effect of the gas-making process is slight, the potential heat of the products of high temperature carbonisation being about the same as that of the original coal, though it should be realised that this equivalence would not be maintained with all coals or at all temperatures. In practice it is of course necessary to expend heat, by combustion of part of the coke, to maintain the coal at the reaction temperature and to make good the losses of sensible and latent heat in the products of the reaction. The present high working-efficiency is a reflection of modern technique with plant which makes possible the recovery and utilisation of a considerable proportion of the heat expended. The hot burnt waste gases derived from the fuel used for heating the retorts are led to an apparatus where the heat is given up to the air entering the furnaces, thereby effecting considerable economy in fuel. Any heat remaining after this in these gases may then be used to generate steam in a special type of boiler, known as a waste-heat boiler. Steam from this source plays an important part in the economy of the modern gasworks, where almost all operations are carried out mechanically. Coal, coke and stores are treated and transported by machinery and the gas itself has generally to be pumped into the supply area by boosters increasing the pressure resulting from the dead weight of the gasholders.

An examination of the Board of Trade Returns relating to authorised gas undertakings in Great Britain reveals that the number of undertakings—706 in 1937—has been showing a steady decrease for a number of years. This is a consequence of rationalisation by amalgamations and absorptions. The recent advent of holding companies also operates in the same way.

The general legislative principles adopted in the control of statutory gas-undertakings were, up to the year 1913, as follows: In the case of gas undertakings controlled by local authorities, a certain minimum illuminating power was prescribed in the Special Act relating to the undertaking, and, in addition, the maximum price which could be charged per 1,000 cu. ft. of gas, and the usual clauses with regard to sinking fund for repayment of capital. In the earlier period, undertakings owned by companies were treated in a somewhat similar manner, their minimum illuminating power and a maximum price being prescribed, and also a maximum dividend payable. It was also usually provided that any new capital raised by such companies must be sold either by auction or by tender and not issued at its par value. Later the maximum price and maximum dividend clauses were dropped in the case of the majority of the statutory companies, and replaced by the adoption of a " standard price " and " standard dividend," and a sliding scale introduced, whereby for each penny the price of gas was reduced below the standard price, an additional dividend (mostly about one-eighth per cent.) was payable above the standard dividend and *vice versa*, if the price of gas increased above the standard, a similar amount had to be deducted from the dividend payable. These sliding-scale clauses, which made it to the interest of the gas companies to reduce the price to its lowest possible figure, had given general satisfaction up to the outbreak of war in 1914, but the great increase in costs of coal and other materials so increased the cost of gas above the standard price that the sliding scale resulted in a very great reduction, and in some cases a disappearance of the dividend payable. As a temporary measure, a short Act was passed in 1917 whereby it was enacted that until the end of the war the sliding scale clauses should not be operative after they had reduced the dividend payable to two-thirds of the standard dividend.

In the years just preceding 1913 a few undertakings had received Parliamentary sanction for the substitution of a calorific-power standard for an illuminating standard. The actual illuminating power prescribed varied considerably with the different undertakings, according to the conditions of coal supply and the character of the demand for gas. The abnormal conditions during the war period 1914–18 saw a material reduction in the illuminating and calorific power of the gas in most cases, partly due to the coal and oil shortage and partly due to the difficulties of plant maintenance. Owing to the abnormal state of affairs, the various statutory stipulations as to the illuminating or calorific power of the gas to be supplied by the various gas undertakings were practically suspended. At the conclusion of the war, the Fuel Research Board of the Department of Scientific and Industrial Research were asked by the Government to report on the matter of the future control of the industry. The recommendations made, modified in certain details after consideration by the Board of Trade and consultation with the gas industry, were made statutory by the Gas Regulation Act of 1920. By this Act, fundamental and far-reaching alterations were made in the conditions under which statutory gas undertakings were to carry on their business.

The most fundamental change made by the Gas Regulation Act of 1920 was that of the basis upon which the gas is charged. In place of a charge based on the volume of gas (1,000 cu. ft.), the charge was made on the number of British Thermal Units contained in the gas supplied or, in other words, on the potential energy contained in the gas. All stipulations as to the illuminating power of the gas were repealed. The unit of measurement is taken as 100,000 British Thermal Units, which is defined by the Act as " a therm." Each undertaking is free to declare what calorific power of gas per cubic foot it will supply, having regard to its local conditions in respect of coal supplies, manufacturing plant, etc., but it must then maintain such declared calorific power as a minimum, under penalty for failure. Supply of gas of a calorific value differing from the declared value may be made only after due notice of such alteration, with liability on the part of the gas undertaking to carry out at its own cost any necessary adjustments of consumers' appliances. In order to ensure that the calorific value declared by the gas undertaking should be maintained, the Act required the Board of Trade to nominate three Gas Referees, one at least to be a person having practical experience in gas manufacture and supply. The principal duty of these Referees was to prescribe times, places and methods for the testing of gas for calorific value, for pressure and for purity in respect of freedom from hydrogen sulphide. The appointment of the gas examiners required to carry out the necessary tests was left to local authorities, a Chief Examiner being appointed by the Board of Trade to decide cases of appeal. A survey made in 1937 showed that 90% of the gas sold in this country had a calorific value of from 450 to 500 B.Th.U. per cu. ft.

The powers of the 1920 Act were amended and extended by the Gas Undertakings Acts of 1929, 1932 and 1934. The first two contain a number of provisions regarding financial powers and extend the scope of authority of the Board of Trade.

The Gas Undertakings Act, 1934, makes a number of important changes in the principal Act and introduces a number of new principles into Gas Law. Under this Act the machinery for carrying out official tests on gas quality is changed. The office of Chief Gas Examiner is abolished and any appeal lies with the Board of Trade. From January 1, 1939, the office of Gas Referees is also abolished and their duties will be discharged by the Board of Trade. Also, by this Act, all non-statutory undertakings making more than 30 million cu. ft. per annum are required to apply for statutory powers. Modified provisions are extended to companies making between 20 and 30 million cu. ft. per annum. Another clause facilitates closer co-operation between undertakings with regard to the giving and taking of bulk supplies.

In recent years the gas industry has been purchasing coal gas from the coking industry, *i.e.* the industry devoted to the manufacture of coke for smelting purposes (*see* COKE MANUFACTURE, Vol. III, 269). This development has been discussed by Philip Dawson (J. Inst. Fuel, 1937, **11**, 1) who points out that improvement in oven design has resulted in considerable economy in consumption of fuel (*i.e.* by-product coal gas) so that the volume of surplus gas has substantially increased as ovens have been modernised. The older type of coke oven, known as the waste-heat oven, which consumes practically all the gas produced, is gradually being replaced by those of the regenerative type. These latter now treat over 70% of the total quantity of coal carbonised by the coking industry. At present about 60% of the gas produced is used as fuel for heating the ovens and 22–23% is absorbed in coke-oven auxiliary plant. Of the surplus the gas industry purchases between 10 and 11%. The actual quantities purchased have been increasing for some years; the figure for 1936 was 24,531 million cu. ft., as compared with 20,474 million in 1935 (16th Ann. Report Secy. for Mines, 1937, 21).

An Area Gas Committee was appointed in 1928 to investigate the practicability of unifying the gas supply in certain specified areas. The Committee reported that such a general scheme was not justified, but recommended that a network of mains should be provided to collect gas from a number of coke ovens in an area between Barnsley and Sheffield. The Sheffield Gas Acts and Orders resulting from this recommendation vested the rights to collect and distribute this gas in the Sheffield Gas Company. This South Yorkshire Gas Grid has made considerable progress. The maximum quantities of coke oven gas contracted for have proved inadequate to meet the increased demands made by industrial consumers and, as a result, additional supplies have been obtained and further extensions are contemplated. The total length of the grid mains in 1936 was about 28 miles (*ibid.*). In 1935, a Departmental Committee of the Board of Trade considered the possibility of co-ordinating the manufacture and distribution of gas in the West of Scotland. The Committee concluded that the establishment of a gas grid scheme over a wide area was not economically practicable, but recommended that certain specified undertakings should take supplies of coke oven gas.

The long-distance distribution of coke oven gas has been extensively developed in Germany where gas derived from pit-head coke ovens in the Ruhr is fed to a large area by means of a network of high-pressure mains. A pipe-line system having a total length in excess of 500 miles is designed to serve an area with a population of about 3,000,000. The Ruhrgas A.G. propose to extend the existing area by the construction of two long-distance high-pressure mains, so that gas made in the Ruhr may be sent to still more distant parts (Chim. et Ind. 1936, **36**, 227). One main will extend from Cologne to Bonn and the other from Siegen to Frankfurt-on-Main. The latter is of particular interest from the technical viewpoint, as it is designed to carry gas at a pressure in the region of 30 atm. In the existing long-distance mains the pressure is from 4 to 6 atm. The potential supply of surplus gas available has been estimated to exceed 230 billion cu. ft. per annum.

The development of the oil fields in the United States has made available very large quantities of natural gas of high calorific value and the long-distance transmission of this gas, whereby it has become available in districts remote from the oil fields, has profoundly affected American, and to a lesser extent Canadian, gas practice. The effect upon gas manufacture can be realised when it is seen that the U.S. Bureau of Mines estimates consumption of natural gas in the United States in 1936, at 2,167,668,000,000 cu. ft. (U.S. Bur. Mines Minerals Year Book, 1937, 1055). This figure is 13% more than that for 1935. In addition to distribution by means of long-distance mains, petroleum gases are liquefied and distributed in cylinders under pressure. This "bottled gas," consisting essentially of propane and butane, is distributed to industrial and domestic consumers, and is of particular value in districts not served by mains. Some 75 million gallons were marketed in 1936 (Gas Age-Rec. 1937, **79**, No. 4, 29). The consumption of liquefied petroleum gases by the manufactured gas industry in the United States is estimated at 9 million gallons for that year. A number of installations to enable the use of propane and butane for stand-by and enrichment purposes have been constructed [*v.* GAS, LIQUEFIED HYDROCARBON (BOTTLE GAS)].

Propane, butane and other saturated hydrocarbons are formed in all reactions resulting from the pressure hydrogenation of coal and coal tar, and some hundreds of road vehicles are already operating satisfactorily in Germany on "rich" gases of this type. Traenckner (Brennstoff-Chem. 1934, **15**, Wirtsch. 94) states that there are six types of gas available in Germany as potential sources of motor fuel. Four of these are derived from the carbonisation of coal, namely, "Ruhrgasol," methane, coke oven gas and town's gas.

The use of compressed coal gas as a motor fuel does not make rapid progress in this country. Problems associated with its use for the propulsion of motor vehicles have been under review by a committee representative of a number of gas undertakings which previously had been individually conducting experiments on the use of gas for this purpose. This committee has published the results of experimental work (The National Gas Council: "Compressed Gas for Motor Transport"). The relative cost of using compressed gas and motor spirit is largely dependent upon the load factor of the compressing plant and of the vehicle storage cylinders. The most favourable economic circumstances for the use of gas occur when there is a fleet of vehicles running a relatively large mileage within a limited radius of a central garage, where the necessary compressing and storage plant can be installed. In a review of the technical application of town's gas, C. M. Walter (J. Inst. Fuel, 1934, **7**, 217) gives running costs obtained with compressed gas and discusses the economics of the subject.

The increasing national importance of liquid fuels in many of the larger countries of the world has been accompanied by efforts to exploit indigenous materials for their production. This trend is particularly noticeable in countries not possessing natural sources of petroleum.

So long as the supply of gas of high luminosity was required, the gas industry, as distinct from the coking industry, was not in a position to extract the benzole from the gas which contains 20–30 times as much benzole per ton of coal as the tar. When the restrictions on the illuminating power of the gas were removed by the Gas Regulation Act, however, a reassessment of the value of benzole in gas form became possible. It still has a comparatively high value in the gas and this may make its recovery undesirable, except under specially favourable conditions. In this country the recovery of benzole at gasworks became general during the war (1914–18) and in 1917 reached a maximum of 5 million gallons, or 16·5% of the total production. Production decreased again after the war, but has increased in recent years as the result of a series of fiscal enactments designed to encourage the production of home-produced spirit.

The Finance Act of 1928 imposed a duty of 4*d*. per gallon on imported spirit and this figure was increased in 1931 to 6*d*. and 8*d*. A few years later this preference for home-produced spirit was guaranteed by the British Hydrocarbon Oils Production Act of 1934, which gives such spirit an advantage of at least 4*d*. per gallon over imported products for a period of 9 years, or 8*d*. for 4½ years. Home-produced spirit is at present free from tax or duty, and as a result the number of benzole extraction plants on gasworks has increased considerably. On the basis of coal carbonised, those works which extracted benzole represented 47·3% in 1936, compared with 44·4% in 1935 (16th Ann. Rept. Secy. for Mines, 1937, **14**, 20). The total output of refined light spirit from gas and tar at gasworks increased by 15·3% during the same period. There is evidence that at present extraction is, in general, more attractive for the larger works than the smaller ones, where the expense of erecting benzole recovery plant is not always considered expedient. Gasworks benzole and its importance as a national source of liquid fuel from indigenous material has been fully discussed in a report to the Minister for the Co-Ordination of Defence ("Sub-Committee on Oil from Coal Report," 1938).

The fact that benzole extraction from coal gas simultaneously removes a proportion of the organic sulphur compounds present in the gas is an attractive feature. Recent researches have demonstrated that with special operating conditions a high percentage of these deleterious substances can be eliminated.

The search for oil from indigenous sources has been in part responsible for the attention which has been directed in recent years to the carbonisation of coal at low temperatures, *i.e.* within the range 500–700°C.

Low-temperature carbonisation is not primarily a gas-making process and the subject, therefore, will not be considered in further detail in this article. It should be realised, nevertheless, that this method of carbonisation receives the close attention of the gas industry. Systems have been, and are being, tried in conjunction with gasworks (*v.* COKE MANUFACTURE, Vol. III, 258, and FUEL, this Vol., p. 364).

Simultaneously with developments in the carbonisation of coal, there has been evolved highly efficient plant for the manufacture of carburetted water gas. This process of gas-making consists in the production of a mixture of hydrogen and carbon monoxide by the action of steam on coke at a high temperature, followed by admixture with oil gas, *i.e.* the product obtained by the pyrolysis of gas oil, whereby it is converted into permanent gases of high calorific value.

The manufacture of carburetted water-gas made considerable headway in the United States and Canada during the first decade of the present century, following the development of oil fields, and in 1910 about 80% of the public gas supplied consisted of carburetted water gas.

This phase was followed, however, by considerable expansion in the use of coke-oven gas for town's supply, and more recently by the development of supplies of natural gas.

In this country, from 1890 onwards, many gas undertakings have also manufactured carburetted water-gas, which is mixed with the coal gas. The use of carburetted water-gas plant as a supplement to a coal gas plant has several advantages which are discussed in detail below (*see* p. 469). It may be stated, however, that its economic value is closely connected with the prices of coke and gas oil, which are subject to fluctuation. For this reason the total quantity made may vary from time to time within relatively wide limits. Production statistics are given in Table III. No figures are available as to the amount of water gas produced by the introduction of steam into the retorts, as the water gas produced by this means cannot be measured separately from the coal gas simultaneously produced, and is in consequence included in the coal gas figures.

GAS COAL.—The type of coal employed for gas-making purposes is normally of the character known as bituminous caking coal, *i.e.* a coal

Table III.—Coal, Coke and Gas Statistics for the Gasworks of Great Britain.

Year.	Coal used.		Coke and breeze made.		Coke and breeze for water gas.	Total coke and breeze sales.			Gas made in authorised undertakings.	
	Authorised undertakings. Tons.	Total. Tons.	Authorised undertakings. Tons.	Total. Tons.	Authorised undertakings. Tons.	Home. Tons.	Exported.[1] Tons.	Imported.[1] Tons.	Coal gas. 1,000 cu. ft.	Water gas. 1,000 cu. ft.
1922	15,907,095	16,556,134	10,475,155	10,862,666	1,057,909	7,737,718	911,307	—	201,963,546	43,946,129
1923	16,460,632	17,202,476	11,098,169	11,508,241	906,717	7,542,867	1,224,302	—	219,756,730	38,347,643
1924	17,329,180	18,104,400	11,657,465	12,085,691	976,366	7,419,305	964,539	34	231,886,036	39,268,220
1925	17,031,172	17,798,725	11,398,382	11.832,842	1,153,413	7,396,681	889,281	—	231,347,681	48,173,291
1926	16,564,172	17,319,274	11,176,933	11,598,249	1,435,572	6,970,733	387,323	117.140	226,572,490	65,309,753
1927	17,703,593	18,456,293	11,939,375	12,364,005	1,034,521	7,591,139	995,364	9,761	246,113,651	47,130,358
1928	17,561,741	18,317,969	11,801,428	12,215,839	979,363	7,699,241	995,868	664	249,835,998	45.211,186
1929	17,886,866	18,609,448	12,032,714	12,411,266	949,235	8,015,437	1,243,377	742	254,797,757	46,349,019
1930	17,669,056	18,371,223	11,912,994	12,316,709	790,086	7,869,419	915,491	552	255,336,236	39,525,450
1931	17,427,481	18,145,372	11,731,796	12,107,372	804,248	7,690,515	977,340	423	254,350,650	40,803,280
1932	17,001,220	17,665,159	11,415,519	11,800,826	745,606	7,430,324	864,785	313	251,018,508	38,468,132
1933	16,714,256	17,355,842	11.090,187	11,472,940	749.151	7,615,487	802,865	585	249,179,563	39,236,880
1934	17,136,702	17,894,665	11,396,237	11,848,654	619,800	7,608,191	813,601	17	257,118,239	32,610,918
1935	17,293,900	18,033,192	11,540,832	11,983,114	639,989	8,042,470	865,163	6,366	260,505,328	32,354,744
1936	18,334,048	19,054,776	12,286,330	12,734,518	545,496	8,417,149	871,304	25,386	274,949,811	27,458,821
1937	18,650,122	19,361,644	12,514,484	12,943,190	529,967	8,478,324	797,610	7,193	279,453,806	27,359,581

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[1] Includes Northern Ireland.

which, in addition to yielding a large volume of gas, also forms a plastic mass during the early stages of the carbonising process and results finally in the production of a coherent coke of good commercial value. The non-caking bituminous coals, even when yielding a large volume of gas, give only a poor coke. These are, therefore, employed only in isolated cases where local conditions are such that non-caking coals are obtainable at a cost sufficiently below that of caking coals to compensate for the lessened value of the coke produced.

Studies by J. Roberts, by E. V. Evans and by others of the formation of coke during the carbonisation process, of the escape of volatile products from the heated coal mass and of the structure of the coke itself, have suggested that in certain circumstances advantages are to be gained by blending the caking coal with a non-caking coal or even with coke breeze. The main object of coal blending is the production of coke of an improved quality, but it may also increase the thermal efficiency of the process. In addition it may facilitate the use of a coal not suitable alone, and it may enable the conversion of a material of low value, such as coke breeze, into saleable coke. The whole subject of coal blending and its rôle in the production of solid smokeless domestic fuel has been dealt with by J. G. King (Trans. World Power Conference 1928, **2**, 348).

The chief supplies of gas coal occur in the Newcastle or Durham district, South Yorkshire, Lancashire, Derbyshire and North Staffordshire. In considering its source of coal supplies, a gas undertaking must take transport costs into account and for this reason will, in general, purchase from the nearest coal-field producing a suitable quality. In the London district, however, and also for the most part in the South and South-West of England the main supply is drawn from the Durham field, the greater distance away of these collieries being more than counter-balanced by the fact that the coal is brought for the greater part of the way by coasting steamers instead of by rail, thus reducing the cost of transport.

The coals obtained from the different seams in the same district, and often even from the same seam, vary considerably in their gas-making properties. Nevertheless, the coals from each district have, as a rule, certain characteristics which distinguish them from those of other localities. This is especially the case with the coals from the Durham field which, for the most part, undergo carbonisation more slowly than the others under similar conditions and yield a harder and denser coke. They also yield a thicker tar of higher specific gravity and, in general, give a somewhat lower yield of ammonia. The North Staffordshire coals also yield gas coke harder than that from Yorkshire, Derbyshire or Lancashire coal.

While bituminous coal is the type of coal normally used for gas manufacture, mention should be made of two other types which have received consideration. Brown coal, or lignite, has been the subject of considerable investigation in Germany where large deposits occur. This is now being used on a commercial scale in that country. It has been necessary to evolve a special technique, one of the main difficulties being a high moisture content. Brown coal from the mine contains 50–60% of moisture and must be dried before carbonisation. When dry it is usually so finely divided that its direct carbonisation presents difficulties and briquetting is generally necessary. The properties of the products of brown coal carbonisation have been discussed by W. Allner (Trans. Chem. Eng. Congr., World Power Conf. 1936, **3**, 47) who gives a description of that industry in Germany.

Cannel coal, formerly carbonised in some quantity, is not now employed to any extent for the manufacture of gas in this country. The coke obtained by the high-temperature carbonisation of cannel coal is in general of inferior quality. Recent investigation of the carbonisation of this type of coal (Inst. Gas Eng. Comms. No. 135, 1936; No. 162, 1937) has suggested the desirability of a national assessment of the available quantities of cannels of sufficiently high quality for gasification purposes.

The classification of coals into groups, such as "gas coals," "steam coals," etc., according to their suitability for specific purposes, is the outcome of accumulated experience in the past and still retains a certain usefulness for commercial purposes. Now, however, that modern knowledge has made it possible to use coals of greatly varying characteristics for the same purpose merely by alterations in technique, such a superficial classification may be misleading. It is more satisfactory to characterise a coal from some fundamental property to which other properties are related. Degree of metamorphism answers to this requirement and has been made a satisfactory fundamental basis for the scientific classification of coals. It is found that the degree of metamorphosis or "rank" of a coal may be indicated by its position on a chart made by plotting carbon content against hydrogen content, or calorific value against volatile matter content (all on a dry, mineral-matter-free basis). On charts constructed in this way, most coals fall within a fairly well-defined band and the characteristics of the fuels change progressively as the band passes from brown coals to anthracites, *i.e.* in the direction of increasing carbon content or decreasing volatile matter content. The well-known classification due to Seyler (Proc. S. Wales Inst. 1931, **47**, 557) is on this basis (*v.* FUEL, this Vol. p. 342).

VALUATION OF GAS COAL.—The simple elementary analysis of a coal, giving the percentages of moisture, carbon, hydrogen, oxygen, nitrogen, sulphur and ash, provides little information as to its value for gas-making purposes. If, however, the figures for moisture and ash be eliminated and the composition be expressed as a percentage of the actual coal substance, it is possible to judge the general properties of the coal from the figures thus obtained. Of greater value is the *proximate analysis*, *i.e.* the determination of moisture, volatile matter, coke and ash and (if required) of sulphur, which is objectionable as an impurity. The quantity of volatile matter, *i.e.* material expelled, excluding moisture, when the coal is heated in absence of air, varies according to the manner in which the heating is carried out, and to obtain comparable results a standard method of heating must be adopted. In addition, the value of a coal analysis depends on the representative character of the sample tested. The British Standards Institution has defined standard methods for the sampling and analysis of coal and coke which are now in general use in this country.

The quantity of volatile matter, excluding moisture, in gas coals usually varies from about 28 to 36% of the undried coal, or from 30 to 40% of the actual coal substance.

The actual results obtainable from a coal sample can be determined only by tests on the manufacturing scale. For this purpose arrangements are made in many works by which beds of retorts can be isolated and the gas passed through special condensing, purifying and measuring plant, and either the whole or an average sample of the gas collected for testing. The coke, tar and ammoniacal liquor produced are also measured in a suitable manner. A special testing works is sometimes erected in large undertakings and by this means quantities of coal up to 20 tons a day can be examined. Small-scale plant, modelled to represent large-scale practice as nearly as possible, cannot be relied upon to give results obtainable in actual practice, as it is not possible to reproduce conditions with sufficient exactitude. Such small-scale plant are, however, of use in giving the *comparative* value of different coals for gas-making purposes, and from tests made with different samples in one and the same plant a fair idea may be obtained of the relative values of different samples. Such apparatus also makes possible a check on deliveries of coal under contract.

THE MANUFACTURE OF COAL GAS.

Briefly, the essential manufacturing processes necessarily involved consist of:

(1) The distillation of coal.
(2) The cooling and condensation of volatile products.
(3) Washing the gas for removal of ammonia.
(4) Purification of the gas from hydrogen sulphide.
(5) Measurement of the gas produced.
(6) Its storage in gasholders.

The plant required consists of retorts set in suitable furnaces, cooling apparatus for the hot gas, exhausting apparatus to pump gas away from the retorts and through the subsequent series of process plant and—eventually to raise the weight of the gas-holders—washers and scrubbers, purifiers, meters and gasholders, together with suitable buildings.

In larger works there may be added to these processes plant for the blending of coals or coals and breeze, apparatus for the removal of cyanogen compounds, organic sulphur-compounds, naphthalene, benzole and water vapour from the gas.

In addition to such plant and apparatus required for the processes there has necessarily to be equipment for the unloading, distribution and storage of coal, for the transport, preparation and storage of coke and other materials, and for the supply and cooling of water. For the driving of these and the other machinery, arrangements are necessary for the supply of steam, hydraulic and electric power. Where carburetted water-gas is manufactured in addition to coal gas, plant for this purpose has to be provided, together with the necessary condensers, exhausters, tar extractors, purifiers and relief holder.

In order to carry out the manufacture under economic conditions, much depends upon the nature and position of the works. So far as the actual site is concerned, a gas-works may only be constructed upon land that has been scheduled by Act of Parliament.

It is not possible to lay down any fixed rules with regard to the selection of sites, as generally only a few possible sites are available relative to the district to be supplied. The site should have a good connection with means of transport, especially with the railway and, where possible, also with water, and even, in certain circumstances, with unloading facilities for direct seaborne traffic, as otherwise the costs for bringing the large quantities of coal required and sending out coke produced are largely increased. It is usually the practice to avoid erecting new works in densely populated areas, but the growth of towns has resulted in many works originally erected in rural surroundings now being completely surrounded by houses.

In the laying out of the site it is impossible to indicate any but the most general rules. The object aimed at is to design the works in such a manner that advantage is taken, where practicable, of existing natural conditions of level and of the relative positions of road, railway, canal or wharf, as the case may be, to facilitate the handling of the raw material and finished products, especially of the coal and coke, which form the largest proportion of these. It is generally considered that two acres of land are required for each 1 million cu. ft. of coal gas produced per day, but on sites in built-up areas where land is scarce and the position favourable to cheap manufacture, this figure has been reduced to 1 acre per million cu. ft. per day by careful choice of plant and skilful arrangement. The provision of sufficient area for gas, coke and coal storage becomes a difficult problem in these cases. As an illustration of the extent to which the ground space required for plant can be reduced, the figures given in Table IV, derived from data of T. Hardie, E. G. Stewart and F. B. Richards, are of interest.

The greater output on a given ground space by the vertical-retort type of plant is noticed if comparison is made with the older horizontal and inclined retorts. Similar developments in washing and purifying plant have enabled the ground space occupied by these units to be reduced. Care must be taken that the plant is such as to allow of the extension of the various portions of the plant without necessitating the pulling down and re-erecting of the original plant in a different position or the undue cramping of the latter.

Most gas-works need to store coke in the open, and it is preferable to locate the retort house on the windward side of the coke store.

TABLE IV.—GROUND SPACE OCCUPIED BY GAS-MAKING PLANT.

Type of installation.	Plant.	Total output therms per day.	Total sq. ft. ground space occupied.	Therms per day per sq. ft. ground space.
Inclined retorts	A (Hardie)	22,338	19,500	1·15
Horizontal retorts	B (Hardie)	34,560	23,400	1·48
Continuous vertical retorts . .	C (Stewart)	50,388	14,212	3·55
	D (Richards)	46,670	13,300	3·50
	E (Stewart)	42,028	13,230	3·18
Intermittent vertical chambers .	J (Richards)	45,060	18,914	2·37
	K (Richards)	34,040	14,432	2·36
Coke ovens	N (Stewart)	85,200	91,800	0·93
	O (Richards)	84,500	62,200	1·35

The total cost of a gas-works including land is roughly £50,000 to £60,000 per million cu. ft. of capacity per day, according to size and location. It may be expected that the cost of the mains, services, meters, etc., necessary to furnish the supply of gas to consumers would amount to double this sum.

Carbonisation of the Coal.

The process of carbonisation consists essentially in subjecting the coal to distillation in closed vessels, whereby it is split up into two portions, namely, a volatile portion which escapes from the retort, and by subsequent treatment yields tar, ammoniacal liquor, and permanent gas, and a non-volatile portion consisting mainly of carbon and the ash of the original coal, which remains behind in the retort as a porous mass of coke. The nature and amount of the constituents of the volatile products, as well as the composition and physical properties of the residual coke, depend not only on the nature of the original coal, but also to a large extent on the temperature employed for its carbonisation and on the manner in which the heating is carried out. The nature of the physical and chemical changes which occur is exceedingly complex, and these, so far as they have at present been elucidated, will be more conveniently considered after a description of the actual process of carbonisation as it is at present carried out in the majority of gas-works.

MANUFACTURE OF GAS IN HORIZONTAL RETORTS.—The materials employed for the manufacture of retorts at the present time consist of fireclay and silica. Under modern carbonising conditions the quality of the refractory must be such that it will withstand working temperatures up to 1,400°, and will not develop serious cracks when subjected to such rapid alterations of temperature as inevitably occur when the hot retort is recharged. Modern practice with its increased through-puts, larger charges and higher carbonising-temperatures, has favoured the use of silica. Again, bigger section retorts are required, and for these fireclay has not the same stamina. As the result of continuous observations on horizontal retort settings in which the average temperature was about 1,050° and the average combustion chamber temperature was 1,325°, S. Hay and A. Edwards (Gas J. 1927, **180**, 538, 612, 808) have shown the advantages of using silica retorts.

The shape of the retorts is long and narrow, the length being about 20 ft. The shape of the cross-section varies, but the majority have a flat bottom and circular top and have approximately the shape of a half-inverted D, ⌓, and are commonly known as D-retorts, the corners between the bottom and the sides being, however, always rounded to facilitate coke removal and to render the retort less liable to crack. The cross-sectional dimensions vary, but are usually from 21 to 26 in. for the major or horizontal axis, and from 15 to 18 in. for the minor or vertical axis. The thickness of the retort wall is 3 in., increased to 4 in. at the ends to facilitate the fixing of the iron mouthpieces and doors.

From 6 to 12 of these retorts are set horizontally in a brickwork arch, being supported by transverse brick walls placed at intervals throughout the length of the retort and extending to the top of the arch enclosing the setting. The method of construction is shown in Fig. 1. The gases by which the retorts are heated circulate around the retorts in each of the vertical chambers formed by the cross walls, travelling first upwards along the inner sides of the retorts and thence over the top of the upper retorts and down the outer sides to the bottom of the combustion chamber whence they are led through channels to a recuperator underneath the setting. In this recuperator, as will be explained later, an interchange of heat takes place between the waste gases leaving the setting and the air entering the setting for the production of, or combustion of, producer gas.

Producers.—The method formerly adopted for heating was that of direct firing, a coke fire being maintained in the centre of the setting below the retorts. With such firing, the heating of the retorts is effected solely by the sensible heat of the products formed by the combustion of the coke, and in order to maintain all the retorts at the requisite temperature it was necessary that the temperature of the hot combustion products should not be below about 1,000° when leaving the setting. In addition, considerable excess of air was required for complete combustion of the coke and this excess air passed away to the chimney at a high temperature. The result was a great waste of fuel, the total consumption of coke amounting to 25–30% by weight of the coal carbonised.

Direct firing has been abandoned in favour of indirect firing by means of producer gas formed from the coke.

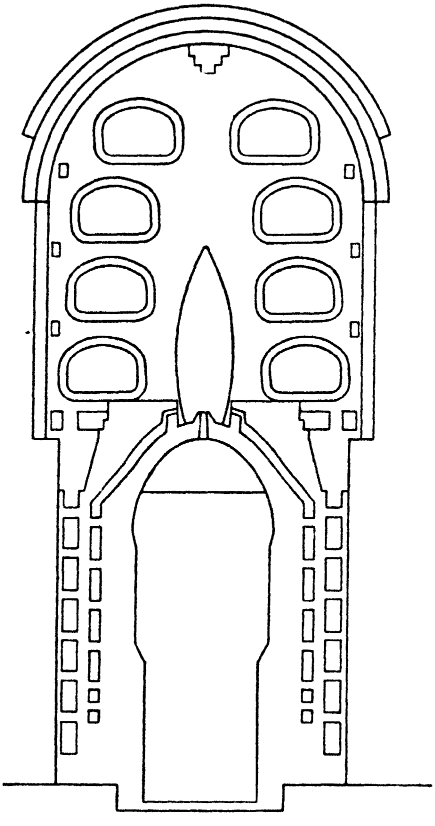


Fig. 1.—Horizontal Retorts, Cross Section.

The original type of producer was a built-in furnace with a bar grate having an area of about 1 sq. ft. per retort. Its defects were that the volume of gas varied considerably according to the presence or absence of clinker on the grate, and that unless frequently replenished with fresh fuel the quality of the heating gas was subject to wide variations as the fuel level rose or fell. It was also difficult to secure a level top to the fuel bed, and, in addition, this type of furnace needed clinkering every 12–24 hours with much loss of fuel in the process. The next stage in development was to remove the bar grate and substitute an inclined step grate. This gave an area equal to 1·6 sq. ft. per retort, and resulted in less clinker formation and less variation in the gas. Another advantage was that, instead of long period cleanings with considerable changes in furnace conditions, this type of grate could be attended to at short intervals of 2 hours, the ash and clinker being removed in small quantities as formed, and much loss of fuel in pan refuse prevented. Still further improvements have resulted in a deepening of the producer so that the store of fuel between fillings ensures a satisfactory fuel bed depth at all times. The grate has been widened so that its area is now 1·75–2 sq. ft. per retort. As a consequence of the larger grate area, clinker formation is reduced to a minimum and the work of ash removal is not only less arduous, but is effected at a lower cost and with less loss of combustible, the fuel thus lost being only 10% of the total pan refuse as compared with 50% with the bar grate.

A similar type of producer with a somewhat larger capacity is used for heating vertical retort settings. The producer gas is removed below the top of the fuel bed in this case.

Producers of the types described are fired with freshly produced coke. In horizontal-retort practice it is usual to discharge the hot coke directly from the retorts into the producer. With continuous vertical-retorts the coke is discharged cool, and the producers of this type of plant are fed with cold fuel. An internal producer of modern type consumes about 3 cwt. of coke per ton of coal carbonised. Where it is not practicable, due to the depth available, to build producers inside the retort house of a sufficient capacity for good working, the producers may be constructed outside the retort house. Though much of the sensible heat of the producer is lost, economies in fuel are effected, due to the better and more regular quality of the producer gas, which is, at the same time, a beneficial factor in the life of the retort. Outside producers may be fitted with mechanical grates and they open up the possibility of the removal of dust from the gas produced which, if it could be achieved, would assist in lengthening the life of the settings. With this system a cheaper fuel is sometimes employed, the gasification of a proportion of fine breeze giving satisfactory results.

The improvements in producer design described above have raised the heating value of the gas from about 70 B.Th.U. to 110 B.Th.U. per cu. ft. (*v.* Fuel, this Vol., p. 367).

Operation of the Setting.—In brief outline, the method of operating the setting is as follows: The hot producer gas passes directly from the producer to the combustion chamber by means of nostril holes at the bottom of each of the vertical spaces formed by the cross walls supporting the retorts. As the producer gas enters the setting, it is met by the stream of secondary air necessary for its complete combustion. This air is introduced by suitable flues so arranged that a supply of air meets each stream of gas issuing from the nostrils. Complete combustion takes place as the streams intermix in their circulation around the retorts. The heat thus evolved raises the temperature of the retorts to the required point.

The waste gases leaving the setting have a high temperature since they must be sufficiently hot to raise the temperature of the last portions of the retort with which they come in contact to the carbonising temperature required. If these hot waste gases were allowed to pass directly to the chimney much loss of heat would ensue. Their temperature on leaving the setting is in the region of 1,000° and they contain energy equal to 50–60% of that produced by the combustion of the producer coke. To effect a partial recovery of this heat the waste gases are passed through a *recuperator*. This consists essentially of a series of flues adjacent to, and separated by a thin brick partition from, a second series through which the secondary air flows on its way to the setting, travelling in the reverse direction to the waste gas stream. Much of the heat is thereby transferred to the secondary air and thus carried back to the setting, enabling a high temperature to be obtained with a lower fuel consumption than would otherwise be the case. An intermittent method for the recovery of heat from the waste gases is in use in the coke-oven industry. This is carried out in *regenerators*, in which two sets of chambers are employed. The hot waste gases being used alternately to heat one set while the air is heated by passage through the other set.

The amount of primary air admitted to the producer and of secondary air to the setting is controlled by suitable slides on the ports of admission and by dampers placed at the outlet of the recuperators. By their adjustment, not only is the total amount of gases drawn through the setting controlled, but also the proportionate amounts drawn into the different parts. By suitable regulation of the primary air slides and dampers the requisite quantity of gas for the proper heating of the setting is made. At the same time the secondary air slides are adjusted to supply as nearly as possible the exact quantity of air required for the complete combustion of the producer gas. With this method of operation, fuel consumption is reduced to about half that which would be required with direct firing.

Until recent years the heat contained in the waste gases was utilised only to the extent indicated above and the gases entered the chimney at a temperature of about 700°. With the object of extracting some of this remaining heat energy, recovery in steam boilers was introduced and is now popular. The earlier installations consisted of an ordinary water-tube or fire-tube boiler interposed between the retort bench and the chimney. The chimney was still used to obtain the necessary draught, but was extended in height to overcome the effects of the lower temperature conditions. It was found, however, in view of the comparatively low temperature head, as compared with boilers using solid fuel, that a specially designed boiler was essential, and the present horizontal fire-tube boiler was evolved. A typical boiler of this form is of, say, 6 ft. 6 in. diameter, 17 ft. between the tube plates, and contains over 280 1¾ in. diameter tubes. With a heating surface of 2,200 sq. ft. such a boiler will reduce the temperature of the waste gases from 800 to 225°C. and evaporate 625 gallons of water per hour into steam at 115 lb. per sq. in. pressure, superheated to 440°F. The efficiency of these boilers is of the order of 60–75%. To ensure sufficient draught through the settings it is essential to provide an induced draught fan, driven either by a steam turbine or by an electric motor. Generally, the higher the velocity of the gases through the boiler tubes the greater is the efficiency of heat transference, but at the expense of higher power costs. The point of balance, therefore, requires careful consideration as the proportion of the output of the boiler used for this purpose may range from 6 to 18%. Where the exhaust steam can be utilised to heat the incoming feed water to the boiler, a high overall efficiency can be obtained if air infiltration can be maintained at a low level, as the steam load on the fan will be such that the whole of the exhaust can then be absorbed. Waste-heat boilers working on horizontal retort settings are fitted with automatic feed-water regulators and are generally provided with superheaters. The results obtained by the employment of these boilers vary from 600 to 1,500 lb. of steam per ton of coal carbonised, according to the design of the setting. Any leakage of coal gas through the retort wall causes a high yield of steam. Expressed in terms of producer fuel consumed, the steam raised is equivalent to 1·8–4·5 lb. per lb. of fuel. Expressed as a proportion of the energy in the producer fuel the heat in the gross steam recovered, *i.e.* including that used for the induced draught, varies from 15 to 45% according to the type of setting. The importance of waste-heat utilisation in a modern gasworks may be gathered from the fact that up to 90% of the steam requirements of a works may be raised by waste heat.

The charging of the coal into the retort and the withdrawal of the coke produced were formerly effected by manual labour. In all works, except the smallest, these operations are now carried out mechanically. A number of types of machine for this purpose have been evolved, but limitations of space preclude anything more than a very general description. In the earlier machines the existing manual method was closely imitated by mechanical means, the charging machine inserting the coal by means of a scoop or similar contrivance and the discharger removing the coke by a mechanically actuated rake. In a more recent machine a stream of coal is projected into the retort, at a velocity such that it is carried to a stop placed at the far end, and then built up evenly. The plan now adopted for coke removal is that of mechanically pushing it out from one end. Other machines effect in one movement the discharge of the coke and the introduction of a fresh charge of coal.

Machine charging makes it necessary that the coal does not contain lumps of too large a size. It is, therefore, dropped into a coal breaker, from which it falls into an elevator and is raised above the retort benches by means of a conveyor into storage bunkers.

The weight of the coal charge naturally varies with the size of the retort. In conjunction with the increases in carbonising temperatures which have taken place in recent years, there has been a tendency to increase the size of the charge in the horizontal retort, for it is now realised that an important condition of coal carbonisation in this type of retort is that the largest possible charge of coal should be placed within the retort compatible with the facilities for heating the coal and with the necessity for providing a free path for the gas to the gas off-take pipe. The temperature in the retort varies in different works from about 900 to 1,250° and the time for the carbonisation of the charge is usually 8–12 hours.

Immediately after charging, the doors at each end of the retort are closed and crude coal gas begins to ascend the off-take or ascension pipes. The gas evolved during the first 2 hours is highest both in quality and quantity. For the remainder of the time the volume and quality steadily diminish, and when carbonisation is nearly complete the gas evolved consists chiefly of hydrogen with some methane and carbon monoxide. E. V. Evans (Royal Society of Arts, Cantor Lecture, 1924) has described this alteration which takes place in the volume of gas evolved from the retort and the gradual decrease in the calorific value of this gas during the carbonising period, and has conveniently expressed the result as shown in Fig. 2. The length, A, of the thermal model represents the time of carbonisation in hours, while the height, B, represents the volume of gas produced per hour and the breadth, C, the calorific value.

In order to obtain a stream of gas which is approximately uniform in quality and quantity, and also to facilitate retort-house working, the retorts are not all charged together, but a certain proportion are charged at regular intervals of an hour or two hours, according to circumstances. By this means the coal in the various retorts is at different stages in the carbonisation process at any particular time.

The coke discharged from the retorts at the end of the carbonising period is quenched with water and removed from the retort house, mechanical conveyors being used for the purpose in modern works.

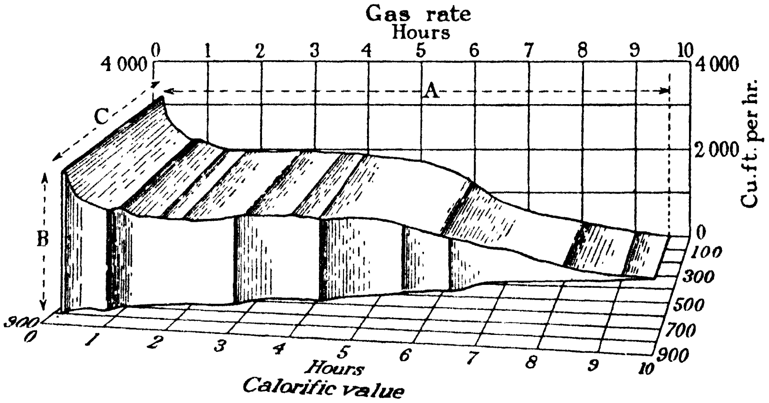


FIG. 2.

The discharge of hot coke from horizontal retorts at a temperature of about 1,000° and its subsequent quenching represents a heat loss equivalent to about 25% of the heat generated in the producer. Attempts have been made to convert this heat to some useful purpose. The method employed in one of these is to place the hot coke in a vessel forming part of a boiler installation, and inert gases are circulated in such a way that heat is transferred from the coke to the boiler water. In Table V (T. Hardie, J. Inst. Fuel, 1927, I, 1) is shown the distribution of heat energy obtained in normal horizontal-retort carbonisation with modern plant, but without taking into account the increases that can now be obtained by absorbing the heat energy contained in the products and in waste heating-gases leaving the settings.

TABLE V.—CARBONISATION OF COAL, HORIZONTAL RETORTS.

	B.Th.U.
Potential energy in coal:	
1 ton at 13,400 B.Th.U. per lb.	30,016,000
Products of carbonisation:	
Gas, 13,160 cu. ft. of 545 B.Th.U.	7,172,200
Tar, 9·35 gallons at 18,500 B.Th.U. per gallon	1,729,750
Coke and Breeze, 14·5 cwt. at 12,284 B.Th.U. per lb.	19,950,000
Heat in combustible products, neglecting ammonia, retort carbon, etc.	28,851,950
Thermal efficiency of conversion =96%.	
Products used on works in process:	
Coke for heating retorts, 3 cwt. at 12,500 B.Th.U. per lb.	4,200,000
Breeze for obtaining power, 1 cwt. at 10,000 B.Th.U. per lb.	1,120,000
Total heat used on works	5,320,000

	B.Th.U.
Products for sale to public:	
Gas, 13,160 cu. ft. at 545 B.Th.U. . .	7,172,200
Tar, 9·35 gallons	1,729,750
Coke 10·25 cwt. at 12,500 B.Th.U. per lb.	14,350,000
Breeze, 0·25 cwt. at 10,000 B.Th.U. per lb.	280,000
	23,531,950

Commercial efficiency of process =78·4%.

Note.—If all power is derived from waste-heat steam, then 1¼ cwt. of breeze are available for sale and the efficiency becomes 82·5%.

Inclined Retorts.—In this type of setting, which is obsolescent, the retorts are inclined at an angle in order to utilise the action of gravity for charging and discharging purposes. The inclined setting is relatively costly to install and has usually a shorter life than a horizontal setting. In addition fuel consumption is higher.

Carbonisation in Vertical Retorts.—Carbonisation in vertical retorts has become increasingly popular during the past 20 years. Among the attractions of this form of carbonisation may be mentioned the successful utilisation of gravity for charging and discharging—without at the same time incurring certain drawbacks inherent in the inclined retort—and the ability to produce simultaneously a proportion of water gas within the retort by the introduction of steam. This form of carbonisation also eliminates disadvantages associated with a large free-space above the coal charge. Furthermore, the water-gas formation in the lower part of the retort reduces heat losses in the discharged coke and assists in the removal of coal gas from the hot zones, thereby protecting it against degradation. In modern vertical retort installations it is the practice to recover sensible heat from the waste gases as steam, not only for use in the retorts but also for generation of power required for driving all the auxiliary plant. These factors contribute to make vertical retort practice an efficient method of coal carbonisation.

Intermittent Vertical Retorts.—The vertical retort, as originally introduced at the beginning of the century, was designed for intermittent carbonisation. That is to say, previous practice was adhered to, in so far that the coal is charged all at once into the retort from an overhead hopper and allowed to remain there until carbonisation is complete, when the coke is discharged by gravity and the retort refilled with fresh coal.

The Dessau vertical retort system, patented by Bueb (B.P. 1393, 1904), represents this type. The retorts are either 4 or 5 metres in length, having an oblong cross-section with rounded corners and are tapered, increasing in size from top to bottom to facilitate the discharge of the coke. 4, 6, 8, 10 or 12 retorts are set in rows of two in a setting, each setting being heated by gas from a separate deep producer capable of being filled much above the point at which the producer gases are drawn off, so that it may run for 24 hours without recharging. The recuperators are arranged on each side of the producers. Fig. 3 gives a vertical section of such a setting and producer, showing the general arrangement of the plant.

As the thickness of the charge is greatest at the bottom, the highest temperature is maintained at this point, with a rather lower temperature in the upper portions where the thickness of the charge is less. The result of this arrangement is that, even at high temperatures, not only is a large yield of gas obtained, but at the same time the tar formed is very fluid and only contains a small percentage of "free carbon." The naphthalene production is lessened, and that of the lower-boiling tar constituents increased, with the result that the naphthalene is sufficiently completely removed from the gas in the ordinary process of condensation without the adoption of any special treatment and, at the same time, the amount of sulphur obtained in the form of carbon disulphide is reduced. The yield of ammonia is higher, and the coke produced is harder and denser than that formed from the same coal in horizontal retorts. These variations are evidence of the fact that less secondary decomposition of the products evolved from the coal charge takes place. Two factors are concerned in this, not only is the free space above the surface of the coal reduced to a minimum, but also there is a path of escape for a portion of the products through the cool central core of uncarbonised or partly carbonised coal, thus avoiding the hot outer layer of coke and the retort walls.

J. S. Thorman (Trans. Inst. Gas. Eng. 1930–31, 364) has described an installation of intermittent vertical chambers which are built of silica throughout their heated height of 19 ft. 6 in., are rectangular in plan, have a major axis of 10 ft. at the bottom and have a uniform taper from bottom to top of the minor axis to ensure unaided discharge of the coke. The coal capacity of each chamber is 3–6 tons. Labour and maintenance costs are low with this type of plant, which has the flexibility regarding gas quality and output characteristic of intermittent carbonisation. The calorific value of the gas produced is determined by the carbonisation period and the time during which the charge is steamed.

Continuous Vertical Retorts.—The object aimed at in this sytem of carbonisation is not only to avoid an excessively heated free space above the coal, but also to render the process a continuous one by the addition of mechanical arrangements whereby the coke is withdrawn continuously from the bottom of the retort, fresh coal being added to the retort at the top to replace the coke withdrawn. In this way the coal travels slowly down the retort undergoing gradual conversion. The conditions in the retort, therefore, remain approximately constant, and the quantity and quality of the gas evolved remain fairly constant, as distinct from the conditions in the intermittently-charged retort where there is a falling-off in both quality and quantity as carbonisation proceeds.

The constant movement of the charge through the retort modifies the conditions of carbonisation. As with the intermittent retorts, the heat penetrates the mass of coal from the periphery and travels inwards, but as the coal is moving constantly downwards, the uncarbonised coal takes the form of a cone, the base of which is at the top and the apex at a point about two-thirds of the length of the retort below. Some of the gas formed escapes through this core of uncarbonised coal, the remainder passing through the surrounding hot coke. The free space at the top of the retort is small.

The continuous system of carbonisation has been worked out chiefly in this country. In the early years of this century results were obtained with the Settle-Padfield continuous vertical retort (B.P. 12552, 1902; 24588, 1903), which showed the possibilities of this form of carbonisation. This was followed by others, notably the Woodall-Duckham (B.P. 16497, 1903 *et seq.*) and the Glover-West (B.P. 23650, 1905 *et seq.*). These two systems in their modern forms will be described in brief outline.

In the Woodall-Duckham system the silica retorts are rectangular in section and tapered. Each bench of retorts is heated by a number of outside producers, the producer gas being taken to the bench by a distributing main and burnt in vertical flues at the sides of the retorts. By means of a second air supply, combustion can take place at two levels. Each retort constitutes a separate unit inasmuch that it has its own producer gas, secondary air and waste-gas dampers, a factor which makes for flexibility of output. The waste gases are collected and taken directly to the waste-heat boiler. The secondary air is pre-heated by circulation around the base of the retorts before rising to the combustion zone through the flues. Steam for gasification and coke cooling is admitted to the coke extractor chambers at the bases of the retorts. Heat economy is facilitated by careful attention to lagging. The waste-gas mains and the producer gas mains are lined with insulating bricks and the side walls and the top of the bench are also insulated.

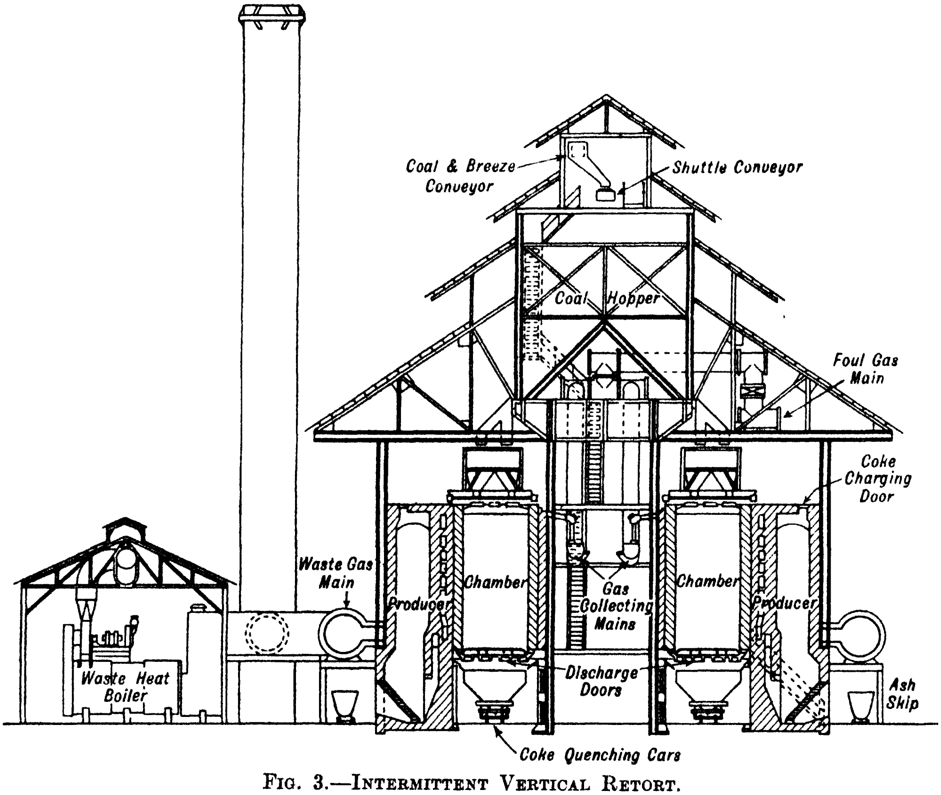


Fig. 3.—Intermittent Vertical Retort.

The Glover-West retort is elliptical in cross-section. The producers, which are built in, one at the base of each setting, supply gas to several horizontal chambers, one above the other, for heating the retorts which pass through the chambers. In this system the retorts are heated most highly in the lower portions, the temperature decreasing towards the top of the retort, round which the heating gases are circulated before passing to the waste-gas flues. Steam is admitted to the coke chambers for coke cooling and gasification. No recuperators are employed, the waste gases passing to collecting flues, whence they are drawn through waste-heat boilers and discharged to the air. The setting is cased in insulating bricks, and the waste-gas flues between the settings and the boilers are brick-lined and lagged. The step-grate producers have no doors at the grate, regulation being controlled by dampers at the entrance to each heating chamber. Fig. 4 illustrates a continuous vertical retort setting.

In the continuous system it is possible and convenient to make efficient use of the sensible heat of the coke by inserting a steam jet at the base of the retort. The steam extracts heat from the coke, reducing its temperature to about 300°C., and simultaneously forms water gas, thereby increasing the make of gas per ton of coal. This steaming process can be extended to 20% of steam, but the first 5% of steam (expressed as a proportion of the charge weight) requires no additional consumption of retort-heating fuel for its decomposition, and results in an increased yield of gas approximating to 10 therms per ton of coal.

For the ideal reaction to take place successfully, the temperature of the reacting substances must be maintained at a minimum of 1,000°C. otherwise the following reaction also appears to take place: $C+2H_2O=CO_2+2H_2$. This leads to the introduction of CO_2 into the gas stream, a condition obviously to be avoided. Furthermore, if the temperature is not sufficiently high, only part of the steam is decomposed and the removal of valuable heat by undecomposed steam causes undesirable complications. The heat required to raise the steam to the optimum reaction-zone temperature is obtained from the coke prior to discharge, an operation which combines heat regeneration with dry quenching of the coke.

It may be mentioned here that attempts have been made from time to time to apply steaming to horizontal retorts, but up to the present it has not been generally adopted. Experiments show that for effective operation it is necessary to have a path above the charge, a tight retort and superheated steam. The quality of the coal greatly influences the results. A discussion on the economics of steaming in horizontal retort practice has been given by G. L. Braidwood (Gas J. 1935, **212**, 701) who emphasises the importance of local conditions.

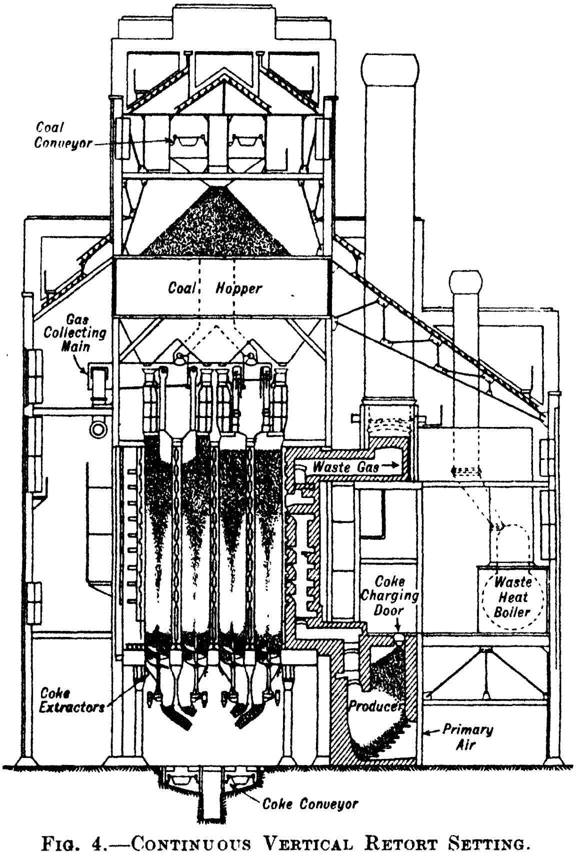


FIG. 4.—CONTINUOUS VERTICAL RETORT SETTING.

From the thermal view-point the continously operated vertical retort is highly efficient. This will be apparent when it is realised that, compared with the horizontal retort, the temperature of the coke discharged is about 1,350°F. lower, and the temperature of the volatile products leaving the retorts is about 200°F. lower. In addition there is reduced radiation from the bench in consequence of the smaller surface area for a given through-put capacity of the plant. Modern practice is to eliminate recuperators and pass all the waste gas directly to the waste-heat boiler.

Air pre-heating is arranged from other sources, such as heat transfer from the retort bases or by circulation through hollow walls of the setting. In this way heat is transferred to the air which would otherwise be lost with the coke or by radiation from the setting. Operation in this way more than doubles the steam yield. Up to 1,500 lb. of steam per ton of coal carbonised can be obtained from waste heat with vertical retorts. After allowing for the induced draught fans, sufficient steam is available, subject to a level load factor, to supply the works' demands. In addition, there is sufficient steam to meet the steam requirements for injection into the retort and then leave a surplus. The recovery of the heat from waste gases has already resulted in the release for sale of large quantities of coke and breeze previously used on the works for steam raising. Waste-heat recovery is discussed by W. Gregson (Trans. Inst. Gas Eng. 1934–35, **84**, 934).

Emphasis has already been laid on the importance which must be attached to the effects resulting from the secondary decomposition of the primary products of carbonisation within the retort. The treatment to which these primary products are subjected in the vertical retort are less severe than is the case within the horizontal retort, where cracking conditions reach a maximum when the retort is operated with light coal charges, *i.e.* with a large free space above the retort. The tar produced in vertical retorts is thin and contains little "free carbon." Naphthalene production is at a minimum and carbon disulphide formation is reduced. Carbonising conditions are also reflected in the composition of the benzole in the gas. Table VI shows analyses of benzoles extracted from gas made in (1) horizontal retorts with a light coal charge, (2) horizontal retorts with a heavy coal charge, and (3) continuously operated vertical retorts.

TABLE VI.

	1.	2.	3.
Weight of coal charge (lb. per cu. ft. of retort space)	28·6	37·0	—
Spirit per cu. ft. of gas (c.c.)	0·790	0·838	—
Unsaturated hydrocarbons as shown by loss on acid washing	4·20	4·40	20·84
Carbon disulphide . . .	1·29	0·79	0·43
Paraffins	2·10	4·39	20·05
Benzene	77·75	68·63	29·56
Toluene	10·44	14·43	9·50
Xylene (to 135°) . . .	1·34	2·32	5·10[1]
Residue	1·92	3·44	13·21
Loss during analysis . .	0·96	1·60	1·31

[1] To 150°.

A high proportion of unsaturated hydrocarbons, of paraffins and of the higher aromatic hydrocarbons reflects the less drastic conditions within the vertical retort.

CARBONISATION IN COKE OVENS.—Attention has recently been paid, notably in Germany and the United States, to the carbonisation of coal for gas-making purposes in chambers of larger capacity and more in accordance with metallurgical coke-oven practice (*see* COKE MANUFACTURE, Vol. III, 260). Where ordinary gas coal is used, the results so far as the quality of gas, tar and ammonia are concerned do not differ materially from those obtained with intermittent vertical retorts. In so far as this country is concerned, it has been shown by E. G. Stewart (Gas. J. 1930, **190**, 754) that coke ovens can be and are being successfully operated with producer-gas firing on gasworks, but that their economic usefulness is limited to the largest works. All charges connected with labour, quenching plant, coke wharf, coal plant, bunker, etc., increase as the size of the unit is diminished. Stewart (*l.c.*) gives the following comparison to show costs of gas making:

	Per therm.
Coke ovens, 1,200 tons per day .	1·804*d.*
Continuous verticals, 646 tons per day	1·815*d.*
Horizontals 480 tons per day. .	2·099*d.*

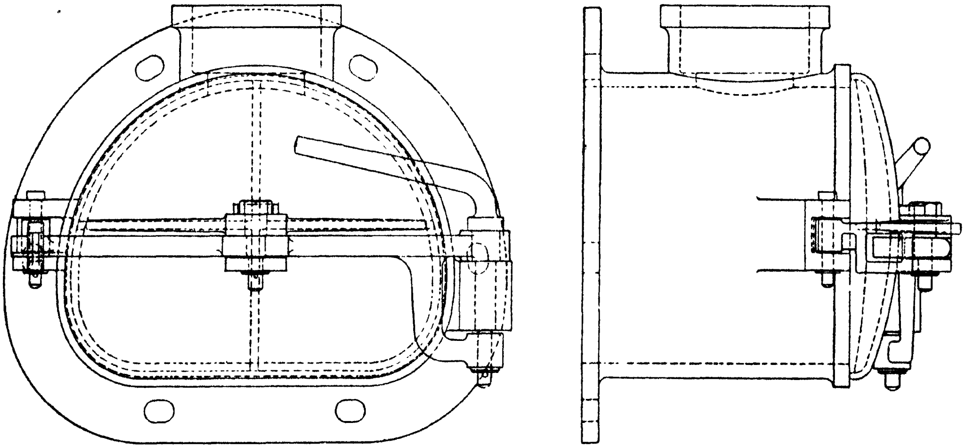


FIG. 5.—SELF-SEALING MOUTHPIECE.

When the daily capacities of the installations are taken into account, the continuous vertical retort is shown to be the cheapest.

A definite outlet for the dense type of coke produced is necessary. Oven coke is suited to large central heating stoves and to other appliances commanding a good draught. It has the advantage of a low ash content and has the ability to withstand transport and storage without breeze production. The use of the open grate and the rapid rise in popularity of the small coke-boiler has created a general preference for a more easily combustible coke. In consequence, coke of the character produced by the horizontal retort and, to a greater extent still, by the continuous vertical retort has been in demand in recent years.

Any examination of the extensive literature on coal carbonisation should include the reported investigations of the Fuel Research Board.

TREATMENT OF THE HOT GASES ISSUING FROM THE RETORTS.—The horizontal retort is fitted with cast-iron mouthpieces having a hinged lid, which can be opened for the purpose of discharging the coke and putting in a fresh charge of coal and then closed so as to form a gas-tight joint. An illustration of a mouthpiece in common use is shown in Fig. 5. In the top of the mouthpiece is cast a socket, into which is fixed a vertical pipe of from 4 to 8 in. diameter termed an *ascension pipe* extending upwards above the brickwork of the setting. By this means the gas is led into the collecting main by way of a seal or valve designed primarily to prevent access of air during those times when the retorts are being charged. These *dip pipes* and so-called "*anti-dips*" will be discussed below. In the case of the vertical retort, the gas is led from the top of the retort to the collecting main in a similar way. A pipe in the top or side of the collecting main conveys the crude gas into the foul main which takes it from the retort house to the condensing and purifying plant.

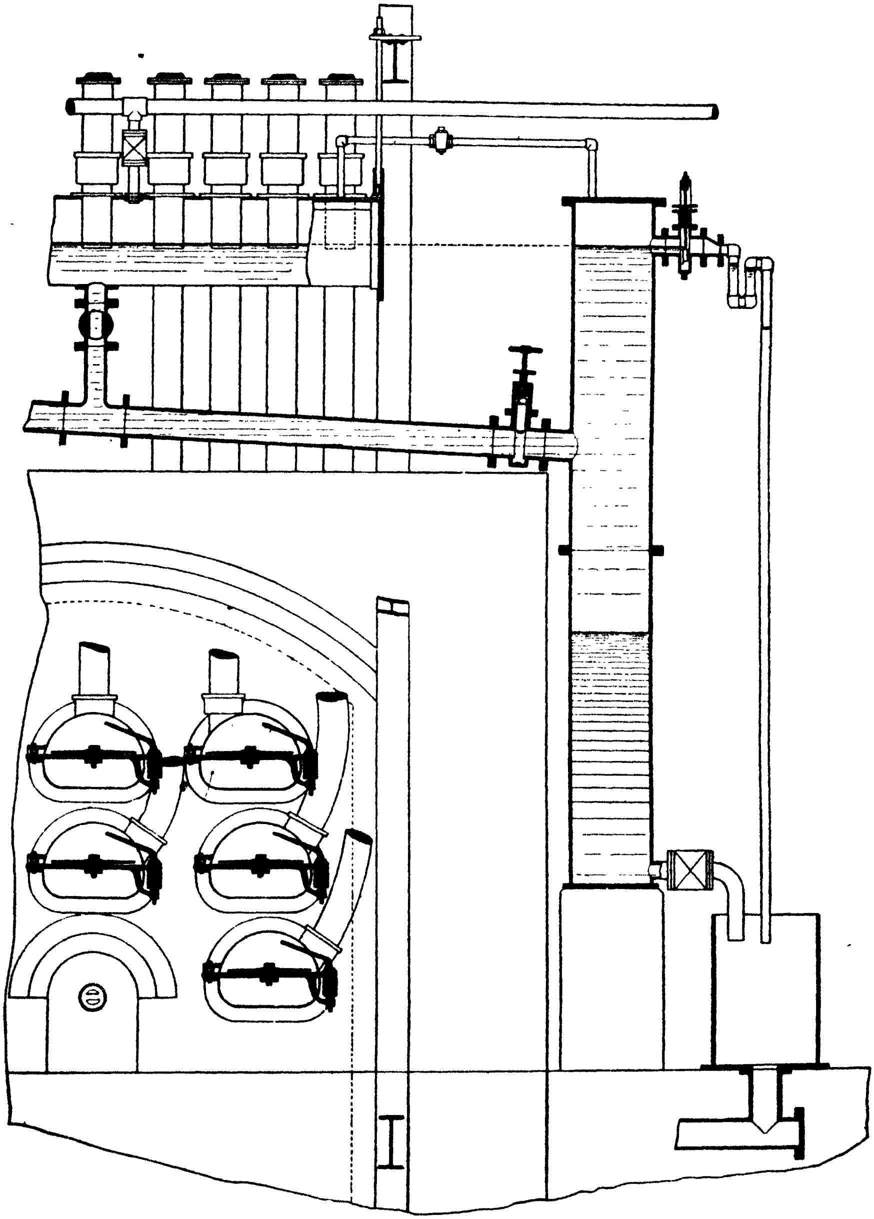


Fig. 6.—Dillamore Tar Tower.

Two types of collecting main are in use, namely, the *hydraulic main* and the *dry main*. In the hydraulic main the tar and liquor condensed from the gas at this point are allowed to accumulate to such an extent that the dip pipes are sealed in the liquid, this seal then forming an automatic vàlve, which allows the gas from the retort to bubble through it into the collecting main, but prevents any gas getting back from that main when the retort lid is open. Where the hydraulic main is employed, it is usual to adopt means whereby the tar and ammoniacal liquor which separate in that main are drawn off separately. The tar is taken away from the bottom as it separates, while the liquor flows away from an overflow, the height of which can be regulated as desired, the object especially aimed at being to ensure that the dip pipes are sealed in liquor and not in tar or varying mixtures of tar and liquor. On some works the Dillamore tar tower, shown in Fig. 6, is in use. This is placed at the end of a bench of retorts as shown and serves a number of beds. The tar pipe runs from the bottom of each hydraulic main to about the middle of the tower, whilst the lighter ammoniacal liquor flows from a side opening near the upper level of the liquid in the hydraulic main to the top of the tower. The latter is also connected by an equilibrium pipe to the top of the hydraulic main, or foul main, the gas pressure in each being thus maintained the same, under which circumstances the upper level of the liquid is the same in both. The condensed liquor flows from the top of the tower over a weir valve, the height of which can be regulated to give any required depth of seal in the hydraulic main. The tar accumulates in the bottom of the tower, displacing an equal volume of liquor, which flows away over the weir valve, and is run off periodically, care being taken that its upper level never rises above the level at which the tar enters the tower. Whilst running the tar off, liquor must be run in from a tank to the top of the tower at a greater rate than that at which the tar is run off, as otherwise the level of the liquid in the hydraulic main would fall, unsealing the dip pipes. A disadvantage of the Dillamore tower is that the depth of seal varies with any sagging of the main.

Sealed mains are fairly common in horizontal retort practice. The alternative method of operation is more usual with dry, *i.e.* unsealed mains, and is usual in vertical retort practice. With this latter type of main the dip-pipes are not sealed in the liquid during the gas-making period, and means must be adopted for disconnecting the retort from the foul main at times of charging. Fig. 7 illustrates one method in use for this purpose. It consists essentially of a double pipe, the outer sleeve of which can be lowered into the liquor to seal the main when required.

Unsealed mains, as distinct from sealed hydraulic mains, may be used with all types of carbonising plant.

In order that the liquor may dissolve the ammonium chloride from the gas and also cool the gas sufficiently to prevent the deposition of tar as pitch, it is necessary that the liquor should have the necessary degree of contact with the gas. With horizontal retorts having sealed dip-pipes, this is obtained by the gas bubbling through the seal. In other cases, where no seals are provided, liquor must be sprayed into the gas.

In those types of plant in which the gas enters the hydraulic main at a high temperature (500–600°), *e.g.* intermittent vertical retorts and coke ovens, considerable evaporation of the circulating liquor into the gas takes place. It is through the agency of this that the gas is rapidly cooled and pitch deposits are prevented. In such systems it is especially important that the circulating tank be provided with an adequate make-up of liquor returned from the condensers, so as to keep the ammonium chloride content of the circulating liquor below about 7 g. NH_4Cl per 100 c.c. of solution.

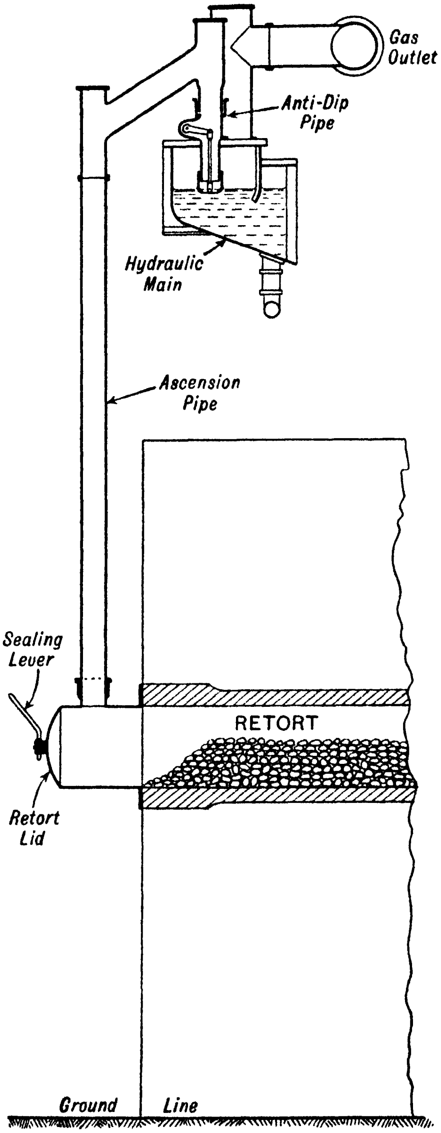


FIG. 7.—HYDRAULIC MAIN AND ANTI-DIP.

For the satisfactory running of the retort house it is essential that the gas pressure in the retort and in the hydraulic or dry main should be under complete control. If the pressure within the retort is allowed to become substantially greater than that in the combustion chamber surrounding it, gas tends to escape through cracks in the retort walls and is burnt around the setting and lost. Analyses of waste gases may, in fact, be used for calculating the thermal equivalent of a coal gas leakage through the retort wall, as has been shown by H. Hollings (*ibid.* 1928, **128**, 924). Again, if the pressure within the retort becomes materially lower than that within the setting, waste gases, consisting chiefly of carbon dioxide and nitrogen, are drawn into the retort and lower the quality of the gas by dilution.

A considerable pressure is required to push the gas through the condensers, scrubbers and purifiers and into the holders. Therefore, in all but very small works, a pump or exhauster is employed to draw the gas from the retorts as it is made and to force it through the subsequent apparatus and into the holders.

In addition an automatic retort-house governor is employed to ensure a constant pull in the hydraulic main, whatever the volume of gas leaving the retorts. At the same time the governor reduces the intensity of the vacuum created by the pull of the exhauster. Retort-house governors are of two types: (*a*) the bell type, and (*b*) the relay type. In the first a system of air floats is employed inside a holder bell, regulation being obtained by direct loading on the bell. In the second a method of counter-balance is used, no air floats being employed. For a detailed description of retort-house governors reference should be made to G. Dougill (Inst. Gas Eng. Comm. 1937, No. 173).

Gas enters the condensers from horizontal retorts at a temperature of about 130°F. With continuous vertical-retorts the dew-point is about 160°F., and with intermittent vertical-retorts and coke ovens 170°F. The high dew-point in the case of continuous vertical-retorts is due to steaming the retorts. The higher dew-point in the case of intermittent vertical-retorts and coke ovens is due to liquor re-evaporated from the circulating systems, consequent upon the high temperature at which the gas leaves the chambers.

Chemical Changes Occurring During Carbonisation.

The ultimate analysis of coal shows it to consist essentially of the elements: carbon, hydrogen, oxygen, nitrogen and sulphur which are combined together in complicated polynuclear aromatic (benzenoid) structures (*v.* Fuel). In the manufacture of coal gas these complex compounds are broken down by thermal decomposition to simpler substances. The products with the simplest molecular structure are found in the gas, while the more complex substances are found in the tar, liquor and coke, the chief by-products of the carbonisation industries.

The following analysis of a typical Durham gas coal, washed fairly free from other substances, gives some idea of the ultimate composition of the coal—carbon 81·64%, hydrogen 5·01%, oxygen 5·78%, nitrogen 1·71%, sulphur 0·91% and ash 3·60%. Although carbon, hydrogen, oxygen, nitrogen and sulphur are the main elementary constituents of coal, other elements capable of yielding volatile carbonisation products may be present in small quantities: chlorine, phosphorus, germanium and arsenic are often to be found in coal together with fluorine, antimony, selenium and boron. Among elements present in coal ash, iron, aluminium, silicon, calcium and magnesium predominate, but traces of other elements such as gallium, vanadium, boron, cobalt, nickel, zirconium, zinc, molydenum, yttrium, silver, indium, thallium, cerium, lanthanum, antimony, tin, lead and bismuth have been identified.

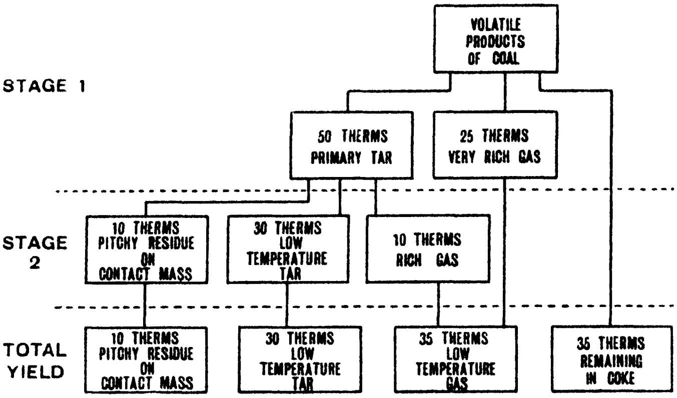
The Action of Heat on Coal: Primary Decomposition of Coal.—The thermal decomposition of coal appears to begin between 290 and 350°C. although water and occluded gases may be evolved below these temperatures and some alteration of internal chemical structures may occur. The first decomposition products are water, carbon monoxide and carbon dioxide, but between 300–350°C. the evolution of hydrogen and hydrocarbons, many of which condense to oily tarry liquids, increases considerably. At temperatures of 200–300°C. the decomposition of sulphur compounds forms hydrogen sulphide: the evolution of ammonia from the nitrogenous compounds appears to take place above 300°C. while the greater part of the oxygen originally present in the coal appears in the products obtained below 500°C.

The initial decomposition is accompanied by a fusing or softening of the coal to form a "plastic layer." This plastic layer is a bad conductor of heat and a barrier to the passage of gases. Gases are formed, however, in the plastic layer and escape in the direction of least resistance, the frothing of the plastic layer causing the cellular appearance of the residual coke. The formation of the plastic layer is, in fact, a characteristic of what is termed a "coking" coal. Non-coking coals yield, under the action of heat, volatile products similar to those obtained from coking coals, but as no plastic layer is formed the residue is either a powder or has the same appearance as the original coal.

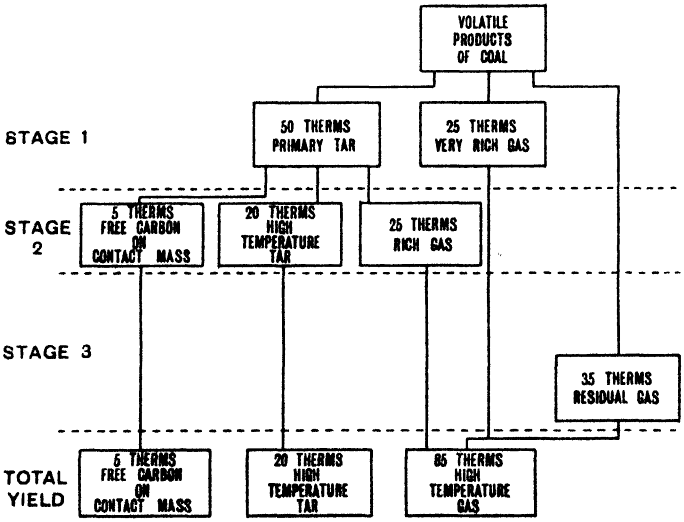
It has been claimed that as much as 70% of the original coal substances may be decomposed below 500°C. and that the formation of free carbon begins at this temperature. Such decomposition is usually termed the *primary decomposition* of coal.

The primary decomposition of coal is best studied by distillation *in vacuo* because there is less probability of secondary changes occurring. Such treatment has shown that hydrogen is a product of the primary decomposition of coal and that the substances obtained in the solvent extraction of coal are decomposition products as they are similar to the tars produced by these vacuum distillations. "Primary" tars of a similar character are produced by heating coal at temperatures below 600°C. under atmospheric pressure. They contain naphthenes and hydroaromatics, olefins, phenol, oxygenated compounds and many complex substances which are benzenoid in structure but rather more complex than benzene itself.

Low Temperature Carbonisation.—When coal is heated in absence of air at temperatures of 500–600°C. the products obtained are largely the results of primary decomposition. The yields of products per ton of bituminous coal (*cf.* Fig. 8) are of the following order: *gas*, 30–40 therms or 4,000–6,000 cu. ft. of calorific value 600–800 B.Th.U. per cu. ft.; *liquid*, 15–20 gallons of liquid which consist mainly of unsaturated paraffin or naphthene hydrocarbons, tar acids and bases, and from which about 3 gallons of light spirit can be obtained; and *solid*, semi-coke, 15 cwt. The composition of the tar and aqueous products from low-temperature carbonisation has been studied by G. T. Morgan and his co-workers (J.S.C.I. 1935, **54**, 19T., etc.) who have shown that phenols and anthracene occur in the products of carbonisation at temperatures as low as 450°C. It would appear that their work confirms the benzenoid structure of coal and correlates with the work of Pictet (Ann. Chim. 1918, **10**, [ix], 249, etc.), and of Juettner and Howard (Ind. Eng. Chem. 1934, **26**, 1115, etc.), on the vacuum distillation of coal.


STAGE 1
VOLATILE PRODUCTS OF COAL
50 THERMS PRIMARY TAR
25 THERMS VERY RICH GAS
STAGE 2
10 THERMS PITCHY RESIDUE ON CONTACT MASS
30 THERMS LOW TEMPERATURE TAR
10 THERMS RICH GAS
TOTAL YIELD
10 THERMS PITCHY RESIDUE ON CONTACT MASS
30 THERMS LOW TEMPERATURE TAR
35 THERMS LOW TEMPERATURE GAS
35 THERMS REMAINING IN COKE

FINAL PRODUCTS ILLUSTRATIVE OF LOW TEMPERATURE CARBONIZATION


VOLATILE PRODUCTS OF COAL
STAGE 1
50 THERMS PRIMARY TAR
25 THERMS VERY RICH GAS
STAGE 2
5 THERMS FREE CARBON ON CONTACT MASS
20 THERMS HIGH TEMPERATURE TAR
25 THERMS RICH GAS
STAGE 3
35 THERMS RESIDUAL GAS
TOTAL YIELD
5 THERMS FREE CARBON ON CONTACT MASS
20 THERMS HIGH TEMPERATURE TAR
85 THERMS HIGH TEMPERATURE GAS

FINAL PRODUCTS ILLUSTRATIVE OF HIGH TEMPERATURE CARBONIZATION

Fig. 8.

Work is still proceeding all over the world on the subject of the thermal decomposition of coal. The complexity of the problem and the methods used by various research workers have been summarised by H. H. Lowry (J. Inst. Fuel, 1937, **10**, 292).

Secondary Decomposition.—The process of coal carbonisation for the manufacture of coal gas is based on the secondary decomposition of the substances formed by the primary decomposition of the coal. Fig. 9 shows a cross-section of a horizontal retort. The combustion chambers round the retort are usually maintained in modern practice at a temperature of about 1,350°C. At the end of a carbonisation the temperature just inside the walls at the crown of such a retort (*i.e.* at point B) may be about 1,150°C. After charging with fresh coal this temperature falls to about 800°C. and then increases by about 30°C. per hour. The temperature of the inner mass of coal rises slowly because the coal and the plastic layers are bad conductors of heat. The temperature of the coal at the point A, for example, may be only 400°C. some hours after charging the retort—such coal will undergo primary decomposition but the products of this decomposition can only escape through the hotter outer layers of the carbonising mass and along the crown of the retort, where they will be subjected to secondary decomposition. All products except those formed near the ascension pipes, which escape with a minimum of secondary decomposition, will undergo a secondary decomposition at temperatures ranging from 800 to 1,100°C.

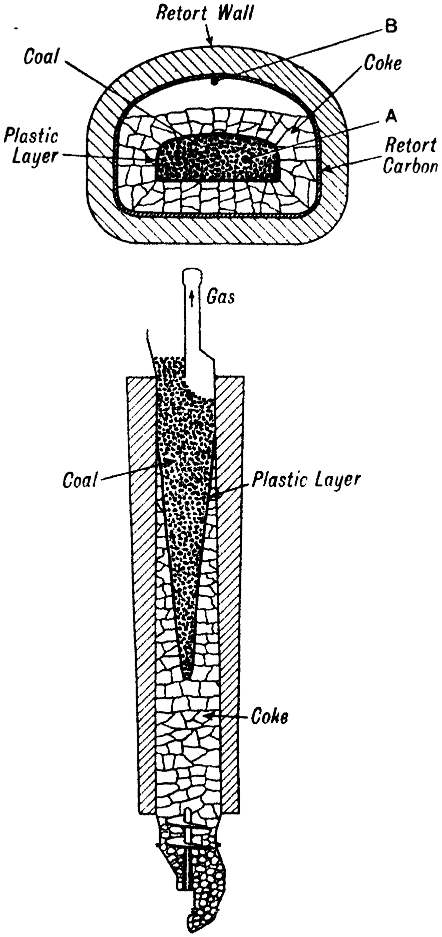


Fig. 9.—Sections of Horizontal Retort and of Continuous Vertical Retort.

The plastic layer will gradually work toward the centre of the charge and coking should be complete at the end of the carbonising period. The latter varies with the size of the retorts but is usually 8, 10 or 12 hours.

The conditions in continuous vertical-retorts are a little different. As cold coal is fed continuously into the top of the retorts there is a cone, as shown in Fig. 9, of lower temperature within the retort and the plastic layer will be almost stationary. The primary products of decomposition evolved at the top of the cone will escape without much further degradation, but substances formed lower down will have to pass either through the coke or through the coal. In the former case they will be subjected to a considerable amount of secondary decomposition. In general, the cracking conditions are not so severe as in horizontal retorts although attempts have been made to control cracking in vertical retorts by providing an empty cracking zone at the top of the retorts. The secondary decomposition conditions in intermittent vertical retorts and coke ovens appear, in general, to be intermediate between horizontal and continuous vertical-retorts.

It will be seen therefore that the process of high-temperature carbonisation will yield a variety of products. Some of these will be the products of primary decomposition, but the majority will have been subjected to a process of secondary decomposition at temperatures in excess of 800°C. In consequence the rates of thermal decomposition of hydrocarbons and the equilibrium conditions existing at temperatures above 800°C. become of interest.

Thermal Equilibrium Conditions at High Temperatures.—The thermal-equilibrium conditions for hydrocarbons at temperatures above 750°C. indicate that only methane and, to a smaller degree, ethylene are appreciably stable. Other hydrocarbons decompose rapidly to yield, eventually, methane and ethylene. Studies of the composition of the gaseous products of high-temperature carbonisation have shown that the concentrations of hydrocarbons are of the following order: methane 24%, ethylene 2%, vapours of benzene and other liquids 1%, ethane 0·8%, with concentrations of less than 0·2% for other hydrocarbons such as propane, propylene, butane, acetylene and butylene. It is apparent, however, that the yield of methane in high-temperature carbonisation is greatly in excess of the thermodynamic requirements for the equilibrium $CH_4 \rightleftharpoons C+2H_2$. At 1,000°C. 0·8% CH_4 is sufficient for this equilibrium, but it has been shown that the decomposition of methane proceeds by a series of steps through ethane, ethylene and acetylene, and that, owing to the retardation of the decomposition of the acetylene by hydrogen, larger amounts of methane are obtained. It would appear that the equilibrium $2CH_4 \rightleftharpoons C_2H_6+3H_2$ is maintained with a very little acetylene and that in consequence larger amounts of methane remain undecomposed so that at 1,000°C., for example, 20% of methane is stable. Equilibrium conditions are more quickly reached at higher than at lower temperatures, and there are some grounds for believing that, apart from equilibria involving carbon, conditions appertaining to the various hydrocarbon equilibria exist in the retorts.

G. Egloff, "The Reactions of Pure Hydrocarbons," (Reinhold Publishing Corporation, 1937), has reviewed fully the present state of knowledge with regard to the thermal decomposition of various hydrocarbons. The original tentative suggestions of Bone and Coward and others (J.C.S. 1908, **93**, 1197, etc.) as to the fleeting existence of free radicles such as CH_3, CH_2, C_2H_5, etc., have been shown to be correct by Paneth (Ber. 1929, **62** [B], 1135, etc.), Rice and others (J. Amer. Chem. Soc. 1931, **53**, 1958, etc.), and there can be little doubt that such radicles play a part in the establishment or partial establishment of various equilibria in the retorts.

The formation of the simpler aromatic-hydrocarbons in the retorts, particularly of benzene and toluene, is of interest in view of the fact that, in general, the more severe the cracking conditions the greater is the yield of these hydrocarbons. Benzole obtained from carbonisation in horizontal retorts is richer, for example, in aromatic hydrocarbons than is benzole obtained from vertical-retort systems. The formation of the bulk of these aromatic hydrocarbons appears to be the result of secondary and not primary decomposition. Many workers since Berthelot have shown that benzene and other aromatic substances can be produced from simpler aliphatic or phenolic compounds, and Wheeler, Wood and others (J.C.S. 1930, 1819) regarded the formation of some of the aromatic hydrocarbons as proceeding in the following stages, ethylene → butylene → butadiene → aromatics.

Besides the equilibria existing between various hydrocarbons and hydrogen, other equilibria are of importance. In view of the modern practice of steaming the hot coke in the retorts in order to form water gas, the equilibrium $CO_2+H_2 \rightleftharpoons CO+H_2O$ has become increasingly important. In order to obtain a maximum of hydrogen and carbon monoxide and a minimum of carbon dioxide the temperature of the coke should be as high as possible (*see* GAS, WATER).

HIGH-TEMPERATURE CARBONISATION.—It has already been seen that high-temperature carbonisation is based on the secondary decomposition of the products of the primary decomposition of coal. The yields of the various substances resulting from the high-temperature carbonisation of 1 ton of bituminous ash-free coal are compared with the products of low-temperature carbonisation in Fig. 8 (*cf.* E. V. Evans, Gas World, 1928, **139**, 205; S. Pexton, J. Inst. Fuel, 1937, **8**, 201). Stage 1 represents the primary decomposition of the coal, stage 2 the mild secondary cracking of the tar and stage 3 the more severe secondary decomposition of the tar together with the removal of 35 therms remaining in the semi-coke to give a total of 85 therms in the gas and 20 therms in the tar.

For a coal containing 8% of ash and moisture the normal complete yields of high-temperature carbonisation are approximately 75 therms of gas (*e.g.* 13,400 cu. ft. of gas of calorific value 560 B.Th.U. per cu. ft.), 18·5 therms of tar (*e.g.* 11 gallons), 16 gallons of ammoniacal liquor, 2 gallons of benzole and 14 cwt. of coke. Many other by-products such as ammonium sulphate, naphthalene, anthracene, pitch, sulphur, benzene, toluene, phenol, etc., are finally obtained. The yields of the various gaseous products during the carbonisation were summarised by E. V. Evans (Royal Society of Arts, Cantor Lectures, 1924), who advocated the use of thermal models such as that shown in Fig. 2 to show the changes in thermal yield and composition of the gas as the carbonisation proceeded.

In the process of high-temperature carbonisation it is essential that the secondary decomposition should not result in what is termed over-cracking. If methane is decomposed to carbon and hydrogen a 36% thermal loss is experienced, since 1 cu. ft. of methane has a calorific value of 997 B.Th.U. and 2 cu. ft. of hydrogen have a calorific value of 638 B.Th.U. Any decomposition reaction resulting in carbon formation will result in a loss of heat and gaseous therms. The tar and gas should be cracked down to the simpler hydrocarbons but not beyond them to carbon. The optimum amount of cracking will be indicated by a maximum of hydrocarbons in the gas. Pexton (*l.c.*) has shown that a figure which he calls the "hydrocarbon enrichment value" can be used to assess the cracking conditions in various carbonising plant. This value ("E") is discussed in detail below (*cf.* "Yield of Gas and By-products," p. 468*d*) but it may be stated here that an increase in the value of "E" indicates a closer approach to the best cracking conditions. "E" can be calculated from the calorific value, the volume of gas made per ton of coal and the concentration of "inerts" in the gas, three simple factors which are easily determined experimentally. In general, the values of "E" for gas from horizontal retorts are higher than those for gas from continuous or intermittent vertical-retorts, a fact which shows the value of the cracking zone at the crown of the horizontal retort. The optimum cracking conditions in high-temperature carbonisation can often be obtained in practice by varying a number of factors. Temperature appears to be the most important of these, but variations in the size of the charge in horizontal retorts can alter considerably the cracking space and the time that the gases are in the cracking zone. The type and size of the coal, the ash in the coal, the pressure in the retorts, the amount of steaming and diluent gases, the presence of more than one ascension pipe, the evenness of the charge in horizontal retorts, and the method of heating and the uniform movement of coal in continuous vertical-retorts will all affect the attainment of optimum cracking-conditions. The blending of coking with non-coking coals or breeze to obtain better cokes or cokes from non-coking materials will also affect the yields of the various products. It would appear that a little over-cracking always occurs at some stages of coal carbonisation as a layer of " retort carbon " or " scurf " gradually builds up on the walls of the retort. A thin layer of this carbon is useful in sealing cracks in the retorts but, from time to time, the retorts have to be left open to the air in order to burn off a little of this carbon. This process is known as " scurfing the retorts."

The following table (Table VII) gives typical analyses of the major constituents and hydrocarbons present in some different types of coal gas.

Table VII.

Gas from	Mixed Durham coal in continuous vertical retorts (steamed).	Mixed Durham coal in horizontal retorts.	Mixed Durham coal in horizontal retorts and coke ovens.	Mixed Durham coal in intermittent vertical retorts.
Combustion chamber temperatures °C. (approx.)	1,370	1,330	1,360	1,310
C.V. of gas, B.Th.U. per cu. ft.	520	567	536	508
Tar yield (gallons per ton)	8·6	10·2	9·7	11·8
Carbonising period (hours)	—	10	10·3 (retorts) 21·8 (ovens)	13
Hydrocarbon enrichment value.	31·9	37·2	34·8	35·5
Per cent. coke oven gas	—	—	26	—

Gas Analysis.

Volume percent. of dry gas.

Constituent.	1.		2.		3.		4.	
Carbon dioxide		1·8		2·1		1·1		1·6
Oxygen		0·5		0·6		0·3		0·0
Carbon monoxide		9·1		6·8		7·4		13·8
Hydrogen		55·4		49·4		53·9		52·8
Methane	23·1		27·6		25·8		20·5	
Ethane	0·868		0·888		0·630		0·963	
Propane	0·077		0·110		0·054		0·157	
Other saturated substances boiling:								
Below 2°	0·117		0·029		0·006		0·028	
From 2 to 25°	0·017		0·003		0·002		0·002	
Above 25°	0·152		0·030		0·013		0·108	
Total saturated substances		24·3		28·7		26·5		21·7
Acetylene	0·072		0·022		0·080		0·014	
Ethylene	1·259		2·384		1·914		1·528	
Propylene	0·166		0·273		0·144		0·229	
Other unsaturated substances boiling:								
Below 2°	0·077		0·061		0·030		0·087	
From 2 to 25°	0·018		0·006		0·014		0·007	
Above 25°	0·149		0·106		0·069		0·115	
Benzene	0·422		0·758		0·748		0·572	
Toluene	0·171		0·167		0·110		0·142	
Xylenes	0·017		0·028		0·034		0·072	
Total CnHm		2·4		3·8		3·1		2·8
Nitrogen (by difference)		6·5		8·6		7·7		7·3
		100·0		100·0		100·0		100·0

Condensation of the Hot Gas.—The combined streams from all the collecting mains of the retort setting unite in a trunk main termed the " foul " main, by which they are conveyed from the retort house to the condensing plant proper, the combined stream having at this point a temperature of 50–60° and still containing much suspended tar fog, amounting in some cases to as much as one-third of the total tar production.

The cooling of the gases to approximately atmospheric temperature is effected by means of either atmospheric condensers or water-cooled condensers. Although types of the former differ in external appearance, the arrangement is in all cases such that the gas is passed slowly through apparatus exposing a large surface to the air, whereby the sensible heat of the gases and the latent heat of the vapours is given up to the air passing over the surface. In the water-cooled condensers water is employed as the cooling medium in place of air. This type of condenser requires a much smaller cooling surface than the atmospheric type, and the temperature to which the gas is cooled can be more readily regulated by controlling the flow of water, provided a sufficient supply of cold water is always available.

Fig. 10 shows the general arrangement of a horizontal atmospheric pipe condenser, the manner of working being readily apparent from the diagram. A modern horizontal water-tube or battery condenser is shown in Fig. 11. This type may be taken as representative of modern practice. The gas enters at the top and flows down one side of the vertical chamber through nests of nearly horizontal steel tubes which are expanded into fixed tube plates, and crossing over at the bottom, passes up to the outlet through similar nests of tubes on the other side of a central division plate. The water flows in series through all the nests of tubes in general direction counter-current to the gas and passes from one nest to the next by way of suitably shaped header plates. Two such units are frequently used in series and connections are provided which enable the installation as a whole to be reversed with regard both to gas- and to water-flow. This type is capable of higher gas- and water-velocities than an older design in which the tubes are placed vertically. H. Hollings and S. Pexton (Trans. Inst. Gas Eng. 1929–30, **79**, 257) have shown that a battery condenser such as the one described, and in which the gas and water velocities are 4·5 ft. per sec. and 0·18 ft. per sec. respectively, requires a cooling surface which is only half that required for the same duty in a vertical water-tube condenser where gas and water velocities are 1·36 ft. per sec. and 0·025 ft. per sec. respectively.

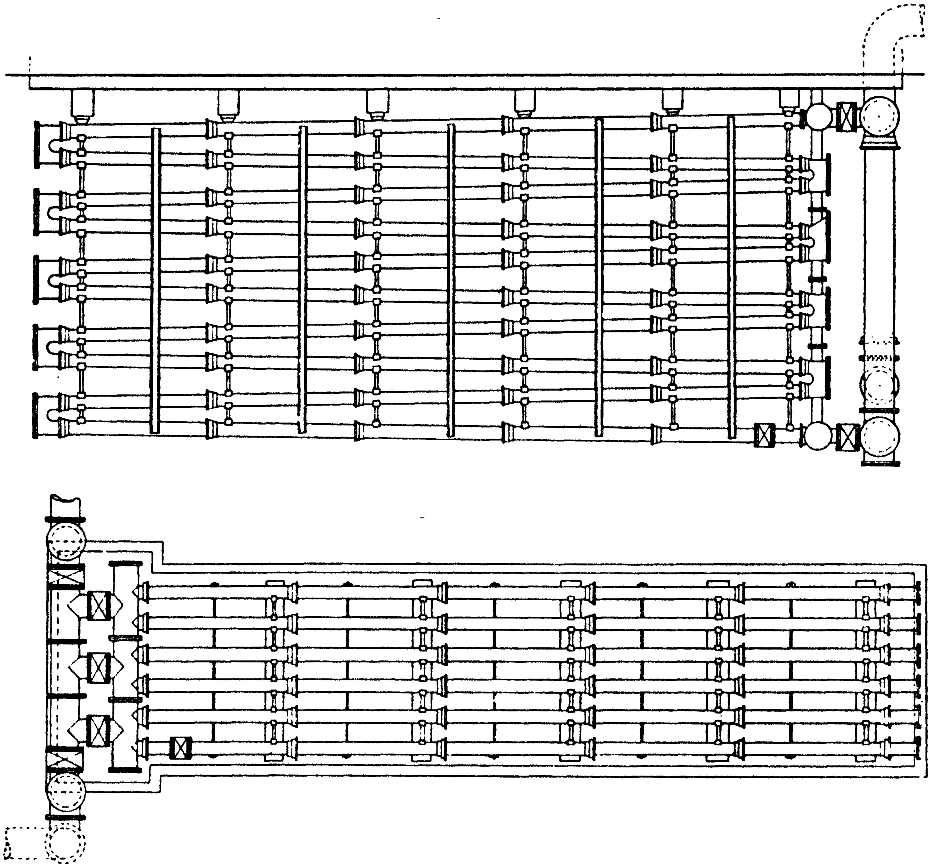


FIG. 10.—ATMOSPHERIC CONDENSER.

When high carbonising-temperatures are employed, especially with certain classes of coal, the tar separating in the cold end of the condenser is apt to become semi-solid from crystallisation of naphthalene. To avoid this it is convenient to arrange the connections and valves in such a manner that the inlet and outlet can be reversed. The end previously cold then receives the hot gas and the thick tar becomes fluid and flows to the tar well, so that by periodic reversals of the stream, blockages from this cause can be largely avoided.

In the early days of gas manufacture the only point considered was the simple cooling of the gas. It was soon found, however, that the manner in which the cooling takes place, *e.g.* the rate at which the gas is cooled and the degree of contact between condensed tar and gas, has a material effect upon the distribution of naphthalene and light oils such as benzole, between the gaseous and liquid phases. This distribution is also affected by the temperature to which the tar is cooled when in contact with the gas. The object aimed at in condensation is not only to cool the gas, but to carry out the cooling in such a manner as to remove the maximum quantity of naphthalene and other high-boiling substances. The importance of the removal of naphthalene arises from the fact that it is a solid at ordinary temperatures and if not removed is liable to be deposited in crystals at a later stage. These difficulties are largely due to the existence of naphthalene in a state of super-saturation in the gas and may be accentuated by bringing tar containing a high concentration of naphthalene into contact with gas having a low concentration. The removal of naphthalene from gas is generally facilitated by rapidly cooling, but it is the usual practice to-day to adopt some more positive oil-washing process for the removal of the last traces of naphthalene.

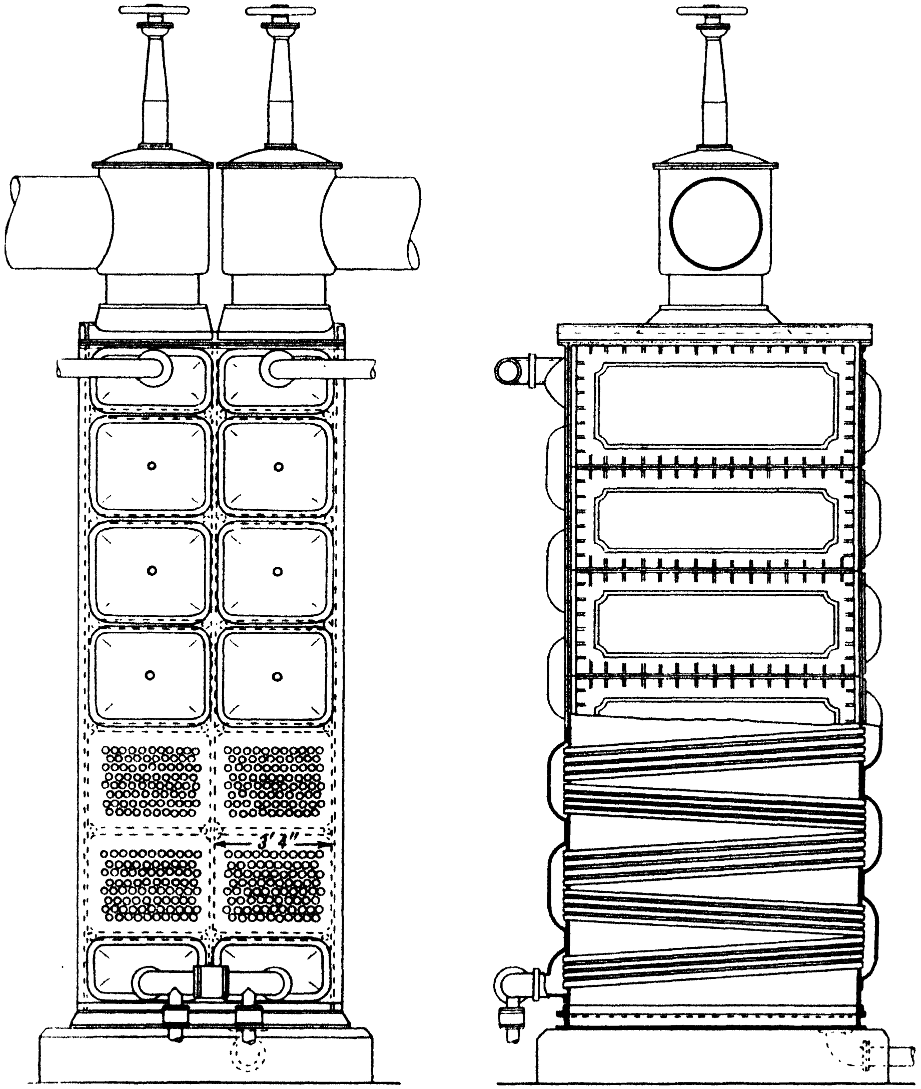


Fig. 11.—Battery Condenser.

The process of gas cooling and the condensation of the tar and liquor should receive detailed consideration for, as has been shown by H. Hollings and W. K. Hutchison (J. Inst. Fuel, 1935, 8, 360), the efficiency of any one of the primary purification processes is very largely dependent upon the efficiency of the one preceding it. The amount of hydrogen sulphide to be removed from the gas depends upon the amount previously removed by the aqueous ammonia liquors, and the efficiency of the ammonia washing plant depends in a marked degree upon the temperature of the gas passing through it and upon the degree of freedom from tar and naphthalene deposits. The temperature and the tar and naphthalene contents of the gas depend in turn upon the efficiency of the condensers.

The amount of water required to cool gas depends upon the temperature of the water, the area of the cooling surface and the rate of heat transmission across the cooling surface. The rate of heat transmission varies with the velocities of the gas and water, the viscosity of the tar condensed and the state of cleanliness of the metal surfaces on both the gas and water sides. Fig. 12 shows the relationship between the area of cooling surface of a modern condenser with horizontal water tubes and the water requirements for cooling saturated gas from the temperatures stated to 60°F., using cooling water at 55°F.

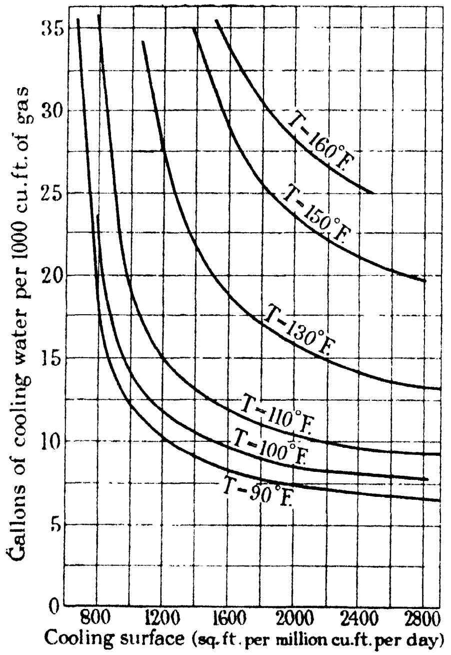


FIG. 12.

Investigations on the establishment of a method for the evaluation of the area of cooling surface required under any predetermined conditions of velocities and temperatures of gas and water have been described by H. Hollings and W. K. Hutchison (*l.c.*). It has frequently been the practice in the past to start from the hypothesis that the quantity of heat transferred across unit area of cooling surface is proportional to the difference in temperature between the gas and the cold surface. The proportionality factor, in suitable units, is the heat-transfer coefficient, and attempts are generally made to relate this transfer coefficient to conditions in the gas, such as temperature, velocity and degree of saturation. In a condenser the temperature of the surface of the tubes cannot be readily determined directly, and results are then given in the form of an overall coefficient, which includes the coefficient for transfer of heat from the tube to the water and is based on the overall temperature-difference between gas and water. This procedure may be justified in a well-designed unit with a low resistance to heat transfer on the water side as compared with resistance on the gas side, so that the temperature of the tube approximates to that of the water flowing in it. The resistance to heat transfer on the water side is not always negligible, however, nor is it a constant proportion of the total. If the rate of heat transfer in a condenser is related not to the difference in temperature between the main body of the gas and the cooling surface, but to the difference between the partial pressure of water vapour in the gas and the vapour pressure of condensed water on the cooling surface, a coefficient is obtained which remains nearly constant over a wide temperature range. Results interpreted on the basis previously referred to give heat-transfer coefficients which increase rather rapidly with rise in the temperature of the gas (*cf.* Cooper, Trans. World Power Conf. Fuel Conf. 1928, 2, 387).

The common sources of water available for use in the condensers are river or canal water, town's or well water, gas-holder tank water and the water used in the boilers for steam raising. The circulation of gas-condenser water through cooling towers does not represent general practice; but it appears to be worthy of consideration. River or canal water is frequently too warm to ensure efficient condensation, particularly in the summer and in those cases where the river or canal is sluggish and is used for condensing exhaust steam from turbines. The water from a gas-holder tank can be used only under certain limited conditions. Town's water and well water are normally below 60°F. and are thus very suitable, though the extent to which they should be used depends on costs. It is often advantageous to use water from two sources, subjecting the gas to a preliminary cooling by means of water from one of the cheaper but less efficient sources indicated above, and then finally cooling with well or town's water which may be subsequently used in the boilers. Its use in the condensers entails no cost apart from water connections. It has been suggested that the reason why this system is not more commonly used is the risk of contaminating the boiler feed water with tar or ammonia through leakage of the condenser tubes. There is no ground for this objection, provided that the pipe which carries the water from the condensers to the boiler feed-tank is vented to air at a point sufficiently well above the top of the condenser to ensure that a greater hydrostatic pressure may be maintained in the uppermost water tubes of the condenser than in the gas space surrounding the water tubes. It must not be overlooked that the dissipation of heat in the condensers represents a thermal loss in the carbonisation process.

During the whole of the condensation, including that occurring in the retort house, there separates from the gas 9–15 gallons of tar per ton of coal (varying with the coal and the conditions of carbonisation) together with 10–15 gallons of ammoniacal liquor. These both flow together to the well or wells, to which any tar and liquor from the subsequent apparatus also gravitate. The condensed water removes a large proportion of the ammonia from the crude gas—usually about half of the 400–450 grains per 100 cu. ft. contained in the gas issuing from the retorts. The ammonia solution also extracts the whole of the hydrochloric acid in the gas derived from chlorine in the coal—and some of the carbon dioxide, hydrogen sulphide and hydrocyanic acid. The liquor obtained in condensation is termed " virgin liquor," that portion formed in the retort house being usually, though not invariably, weak and containing from 0·5 to 1·5% of ammonia, whilst that from the condensers is more concentrated and may contain 4% or more. The cooled gas mostly contains some 200 grains of ammonia and 50–100 grains of hydrocyanic acid per 100 cu. ft., some 1–2% of hydrogen sulphide and 1–3% of carbon dioxide. In addition, there is also an appreciable amount of tar fog, which has not been removed from the gas in its passage through the condensers and which, if not previously extracted, is deposited in the subsequent purifying apparatus, rendering them much less efficient.

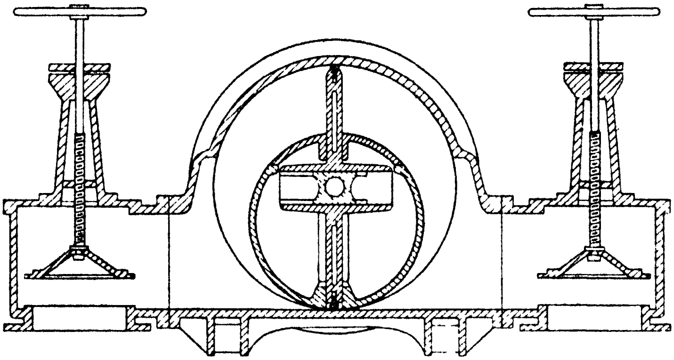


Fig. 13.—Beale Gas Exhauster.

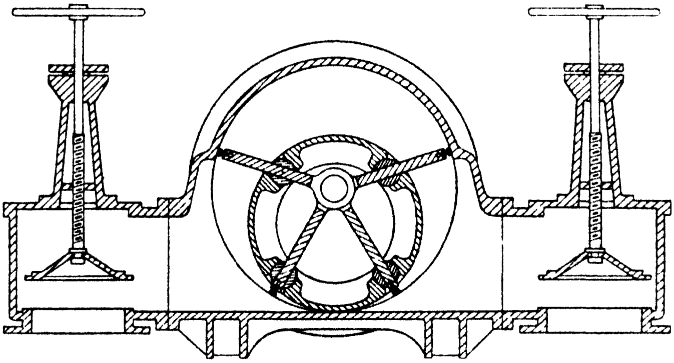


Fig. 14.—Four-Blade Gas Exhauster.

Exhausters.—The gas pump or exhauster has been an essential piece of gas-works plant ever since the days when the industry changed from the cast iron to the fireclay retort. It is called upon to exhaust the crude gas from the retort house at a suction of 4–10 in. water gauge, and to drive the gas through the subsequent series of purification plant and ultimately to raise the gas-holder bell, which necessitates a back pressure of 25–60 in. water gauge.

The types of machine which are now used for this purpose are :

(1) Slow speed rotary.
(2) Turbo.

The slow speed rotary machines take one of two forms. The first is the Beale type or later developments of it, as shown in Figs. 13 and 14. These machines operate at approximately 60–70 revolutions per minute. The second type of rotary machine is a development of the Roots blower, consisting of two double lobe impellers. This type of exhauster, which in its modern development is the Connersville, is shown in Fig. 15. The speed varies between 150 and 350

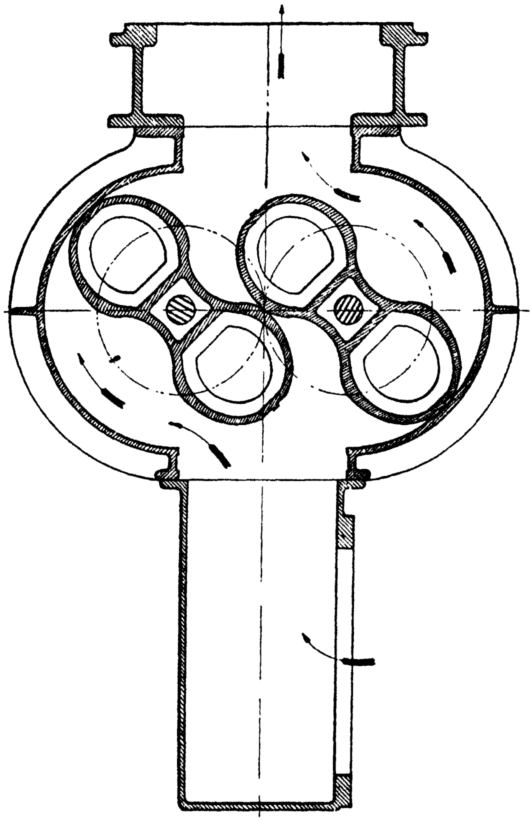


FIG. 15.—CONNERSVILLE GAS EXHAUSTER.

revolutions per minute according to size. In larger installations at the present time the preference is now being given to the high-speed turbo-exhauster of the Rateau type which operates at several thousand revolutions per minute. There is also the further type of turbo machine with star-shaped impeller running at 8,000–10,000 revolutions per minute (Fig. 16). The advantage of the two last types is that in addition to acting as gas pumps they also act as very efficient tar extractors.

The position of the exhauster is entirely arbitrary, but it is normally found in sequence between the condensing and washing plant, but it can be placed prior to the gas condensers and immediately upon the outlet of the retort houses. In any case the plant has to be equipped with delicate governing arrangements to take account of the varying flow of gas and to maintain constant suction. The normal power for driving is steam on account of the improved reliability in operation obtained thereby, but electricity can be and has been used as a motive power. On the largest gas-works the addition in recent years of a number of refinements in the purification process has so increased the back pressure against which the exhausters have to pump that supplementary exhausters placed after the oxide purifiers have been installed. These supplementary exhausters are usually of the fan type, capable of giving a differential pressure of 20 in. of water gauge.

EXTRACTION OF TAR FOG.—To eliminate the remaining tar fog from the cooled gas, many mechanical devices have been evolved, based on impingement of the gas upon surfaces or on centrifugal action. A common method in English works is to combine the removal of the tar fog with the removal of the last traces of ammonia, in an apparatus which breaks the gas up into a number of fine streams which are bubbled through ammoniacal liquor. This serves the double purpose of removing tar fog and of strengthening the weak liquor which is fed into the apparatus. An efficient apparatus of this type is the Livesey washer, the essential feature of which is shown in Fig. 17. This washer consists of a parallel series of troughs arranged in a cast-iron rectangular vessel, the lower portions of which are perforated with holes $\frac{1}{20}$ in. in diameter, as shown, this portion being sealed in ammoniacal liquor. The gas entering at the top passes down between the troughs and forces some of the liquor through the holes into the interior of the troughs, thus unsealing the holes, through which the gas then bubbles, as well as through the second perforated plate across the width of the trough. The liquor in the trough is broken up into foam and effects the removal of the tar fog and also ammonia, the washed gas passing away through the open end of the trough to the gas outlet. With

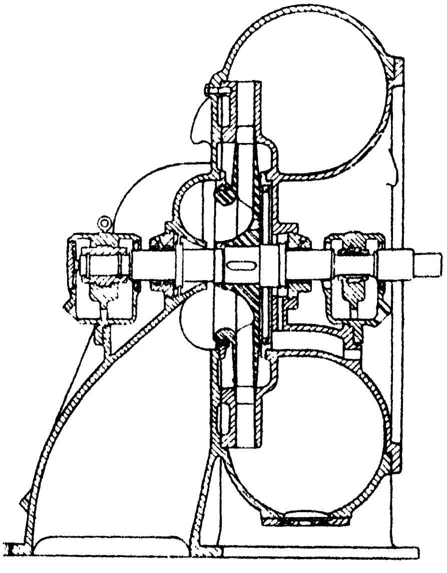


FIG. 16.—TURBO EXHAUSTER.

proper working the amount of tar fog can be reduced to below 10 grains per 100 cu. ft.

The procedure which has been adopted by the gas industry in the past has been largely determined by the fact that tar will not adhere effectively to baffling surfaces unless the temperature of the gas is reduced to the region of 100°F. Cooling of the gas to this temperature is thus essential in order to effect an efficient tar-separation by mechanical means. The electrical precipitation of tar is receiving considerable attention, and it has been shown that Cottrell's process may be applied to the removal of tar fog from coal gas at all temperatures up to 160°F., the maximum temperature of the gas at the outlet of the hydraulic main. Fig. 18 shows a precipitator of this type as used in a gasworks.

Ammonia Recovery.—To complete the removal of the ammonia the gas is now washed with water or weak ammoniacal liquor. One of the oldest forms of apparatus for the purpose was the tower scrubber, in which the gas passed counter-current to a stream of water in a tower filled with coke, wooden boards on edge or other material which would give a large surface area. In place of these towers rotary washers are now largely employed. Several efficient types are in use, one of which, the Kirkham washer, consists of a horizontal cylindrical vessel, divided internally into compartments by vertical plates which have openings, where necessary, to allow passage of the gas. In each compartment is a disc keyed to the central revolving shaft. This disc, with the exception of the central portion, is fitted with bundles of thin wooden boards or sheet-iron plates, fixed together in such a manner as to allow free passage of the gas over their surface. The gas, in traversing the apparatus, passes over this surface, which is kept wetted by revolving through the liquor in the bottom of each compartment, and effects the removal of the ammonia. The Holmes washer (Fig. 19), which is largely in use, resembles the foregoing in main outline, but special brushes are used to form the necessary washing surface (*cf. also* Absorption).

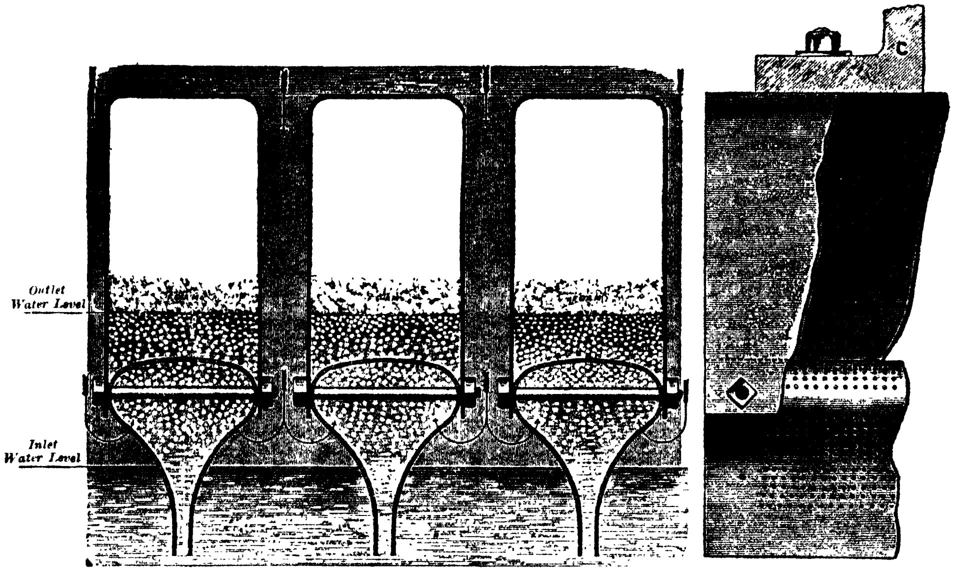


Fig. 17.—Livesey Washer Diagram.

It is now realised that important economies can be effected by reducing the quantity of water used. The use of weak liquor as the scrubbing medium, to the partial or complete elimination of water, is dependent upon efficient cooling of the gas and upon the provision of washers of adequate capacity. In some cases, nevertheless, the total capital charges in respect of any necessary additions to condensing and washing plant may be more than offset by the visible economies resulting from the production of a stronger liquor, without any reference to the other advantages associated with the use of efficient cooling plant.

A suitable medium for the replacement of water may be obtained by fractional condensation of the virgin liquor (Trans. Inst. Gas Eng. 1927–28, 495). The weak ammoniacal liquor which condenses in the first part of the condensers is not allowed to mix with the stronger liquor condensing further down, but is drawn off separately. The strong fraction is passed to the strong liquor tank and is not re-circulated, but the excess weak liquor is passed through a cooler and then to the washers. In order to obtain a strong liquor it is necessary to ensure that the temperature of both gas and liquor in the ammonia recovery plant is as low as possible, and that the retort-house circulation system and condensers are so operated that the ammonia concentration in the gas entering the washers is also as low as possible. In the recovery of ammonia liquor on the gasworks and its conversion to sulphate of ammonia there are several expenses which are a simple multiple of the volume of liquor to be handled. The extent of the economy which may be effected by reducing the quantity of water used is made evident in the 1st Report of the Ammonia Sub-Committee of the Institution of Gas Engineers (1929).

The economics of ammonia recovery on the gas-works has been seriously affected in recent years by the development of the relatively cheap method of producing ammonia synthetically and by an increase in the cost of conversion of gas liquor into sulphate. In consequence considerable attention has been given to means for increasing the net value of ammonia on the works. The adoption of a method whereby the gas liquor is concentrated on the works and then despatched to a central plant where it can be worked up, has proved to be a valuable development.

It will be appreciated that in any consideration of the performance of plant in which ammonia is recovered from coal gas in the form of an aqueous solution, it is very desirable to have exact data concerning the distribution of ammonia between gas and liquid and to know the influence of the presence of carbon dioxide and of hydrogen sulphide in the system. The ammonia and carbon dioxide vapour pressures of solutions of these two gases have been determined by S. Pexton and E. H. M. Badger (J.S.C.I. 1938, **57**, 106) at various temperatures. When hydrogen sulphide is added to such solutions it combines with half its equivalent of ammonia, and the resulting hydrosulphide has no effect on the vapour pressures due to the remaining ammonia and carbon dioxide. The vapour pressures of aqueous solutions of ammonia and carbon dioxide are increased by the addition of ammonium chloride. The virgin liquor condensed from horizontal retort gas contains less carbon dioxide than does that from vertical retort gas. Because of this deficiency of carbon dioxide, the virgin liquors obtained by the method of fractional condensation, described above, is a less efficient washing medium when derived from horizontal-retort gas than those obtained from vertical-retort gas. This inferiority may be rectified by the addition of a small quantity of carbon dioxide to the liquor prior to its use in the washer.

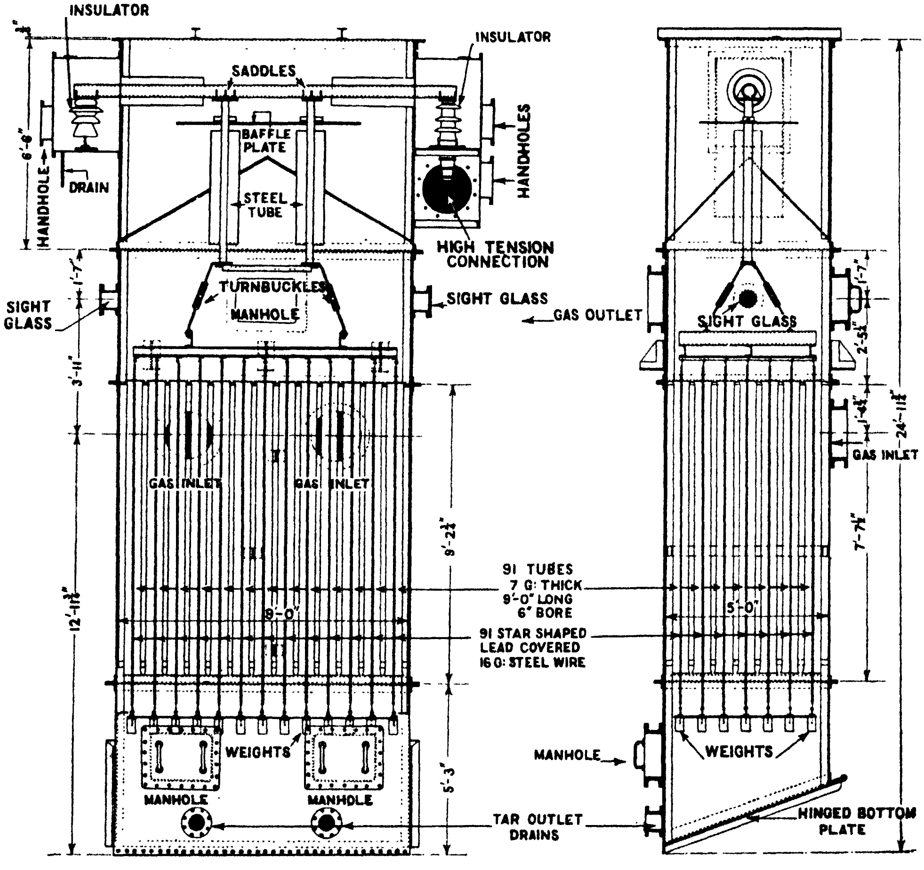


FIG. 18.—COTTRELL PRECIPITATOR DIAGRAMS.

The process described above, in which the gas is cooled by passage through condensers before scrubbing out the ammonia, is the only one in general use in the gas industry and is known as the indirect process. Two other methods of ammonia recovery—the direct and semi-direct processes—are in use in the coke-oven industry (*v.* COKE MANUFACTURE AND THE RECOVERY OF BY-PRODUCTS). In the direct process the gas is freed from tar fog and then passed directly to the saturator at a temperature of about 75°C. The semi-direct process consists essentially in cooling the gas below its dew-point (25–45°C.) and then re-heating to about 60° before passage into the saturators. It is claimed that the cooling is necessary for the satisfactory removal of tar and the production of good quality sulphate of ammonia. The relative merits of these three methods of ammonia recovery have been considered by the Ammonia Sub-Committee of the Institution of Gas Engineers (2nd and 3rd Reports, 1929, 1930). The opinion is expressed that there is little likelihood of any drastic change in present gas-works practice being adopted with economic success in the immediate future.

In the event of either the semi-direct or the direct process being adopted by the gas industry, the chief difficulty would be that existing condensing and recovery plant would have to be scrapped and a completely new type of plant, involving fresh expenditure, be adopted.

The development of the manufacture of concentrated gas liquor and its treatment at central chemical works is described by P. Parrish (Inst. Gas Engrs. 1939, Comm. No. 213).

The disposal of waste effluent-liquors from ammonia stills is a matter which requires close control and considerable attention has been given to the subject by the industry. A recent work by A. Key (Gas Works Effluents and Ammonia, Institution of Gas Engineers, 1938) reviews 12 years' systematic work.

HYDROGEN SULPHIDE REMOVAL.—The crude gas leaving the retorts contains hydrogen sulphide in a quantity depending upon the sulphur content of the coal and the method and condition of carbonisation. With an average Durham coal containing 1·5% of sulphur, carbonised under normal high-temperature conditions in horizontal retorts, the hydrogen sulphide content of the gas entering the condensers will be between 550 and 650 grains per 100 cu. ft., *i.e.* about 1% by volume. Of this some 10–15% is removed from the gas by combination with ammonia, about 500 grains of hydrogen sulphide per 100 cu. ft. remaining to be removed from the gas leaving the ammonia washing plant. Other impurities are also present, namely, 1–3·5% of carbon dioxide, together with smaller amounts of other impurities including 10–80 grains of sulphur per 100 cu. ft., as organic sulphur compounds, chiefly carbon disulphide, and from 40 to 80 grains of hydrogen cyanide. Of these the hydrogen sulphide must be removed to an extent which is practically complete. Stringent statutory provision is made to this effect in Acts of Parliament controlling gas undertakings. The carbon dioxide is not in itself deleterious, but was formerly frequently removed owing to its adverse effect upon illuminating power. The hydrogen cyanide is extracted more or less completely during the removal of the hydrogen sulphide.

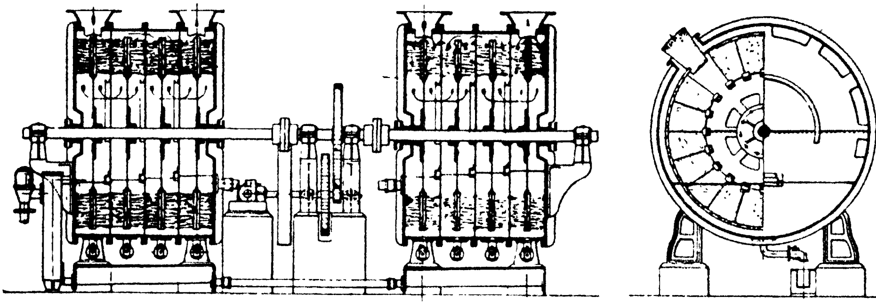


FIG. 19.—ROTARY SCRUBBER WASHER.

It should be noted that in American and Continental practice the hydrogen sulphide concentration is frequently as low as 300 grains per cu. ft. This fact must be borne in mind when comparing designs of plant and costs of purification. On the other hand, gas obtained from other coals or by the low-temperature carbonisation of coal may contain much higher concentrations.

The purifying material employed for the removal of hydrogen sulphide is moist hydrated oxide of iron, the naturally occurring bog-iron-ore being used largely for the purpose. This contains a sufficient amount of fibrous organic matter to render the mass porous and allow of the passage of the gas through it. Where artificially prepared ferric hydroxide is employed, it is mixed with a filler such as saw-dust or wood chips, to give the required porosity.

The material is charged in even layers into rectangular cast-iron or reinforced concrete vessels containing wooden grids to carry the oxide, the thickness and number of the layers varying according to the size of the purifier. In the older type of purifier the lid was rendered gas-tight by the provision of vertical sides dropping into a water lute cast around the periphery of the purifier. So long as the pressure of the gas within the box does not exceed that equal to the depth of the water seal, no gas can escape. As, however, cases have occurred in which the gas has escaped through the seal, the present practice is the adoption of luteless lids which are bolted to the purifier and made gas-tight by the insertion of a rubber joint between purifier and cover. A modern purifier of this type is shown in Fig. 20.

The purifying medium may be regarded as a mixture of ferrous and ferric hydroxides on which the hydrogen sulphide in the gas reacts in the following ways:

(1) $Fe(OH)_2+H_2S=FeS+2H_2O$.
(2) $2Fe(OH)_3+3H_2S=Fe_2S_3+6H_2O$.

The reactions between the iron oxide mixture and the impurities in the gas will, in the absence of added alkali, gradually develop acid conditions. Such conditions retard the absorption of hydrogen sulphide and more especially hydrocyanic acid. Moreover, a slight alkalinity considerably assists the absorption of both these substances. It is usual, therefore, to admit a small quantity of ammonia to the boxes; up to 4 grains of ammonia per 100 cu. ft. is usually sufficient. Larger quantities affect the nature of the products derived from the hydrogen cyanide. It is now recognised that moisture also plays an important part. R. H. Clayton, H. E. Williams and H. B. Avery (Gas. J. 1931, **196**, 311) have found that air-dried oxide is very inefficient as an absorber of hydrogen sulphide or hydrogen cyanide from coal gas and that moisture is essential for the reactions between these impurities and the oxide. Conditions which favour the effective removal of hydrogen cyanide from the gas are ideal for the removal of hydrogen sulphide. In several works in England it is now customary to remoisten the oxide *in situ* by opening the box and spraying the oxide with water until a sufficient degree of humidity is reached. This operation may be repeated several times before the box is emptied. At other works wet steam is introduced for this purpose.

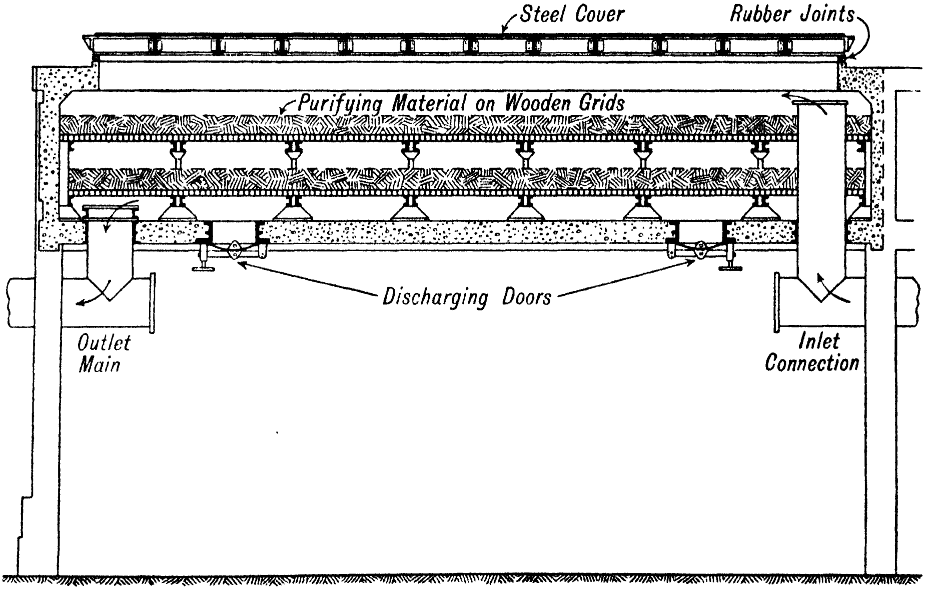


Fig. 20.—Diagram of a Modern Purifier.

When the mass has ceased to absorb hydrogen sulphide it may be removed from the purifier and spread out to give exposure to the air. By this means the iron sulphides are oxidised, reforming hydroxides, with separation of free sulphur. As soon as the revivification is complete the mass can be returned to the purifier for the extraction of further amounts of hydrogen sulphide, this alternative process of fouling and revivifying being continued until the mass contains 50–70% of sulphur. It may then be sold for its sulphur content, being used chiefly for the manufacture of sulphuric acid.

As the crude gas entering the purifiers always contains some inherent oxygen, revivification takes place to some extent by this means. Nevertheless, reliance on this source of oxygen alone would necessitate frequent removal of the oxide mass from the box. Under modern conditions, additional air is introduced into the purifiers with the gas, so that the life of the oxide in the box is increased and the number of changes for external revivification, and consequently the cost for labour, considerably reduced. A limit to the amount of air added is fixed by the fact that excess oxygen and nitrogen remaining in the gas affect its quality. Also, if the excess of oxygen reaches a certain concentration, the separated sulphur may even fire in the purifiers and, apart from the damage caused in the box, the gas may be contaminated with sulphur dioxide. The temperature of the gas passing through the box should not fall below about 15°, since the action of the oxygen then becomes too slow.

The purifiers are usually worked in sets of four, the connections being so arranged that the gas can be allowed to enter any box and then pass in series through the remaining boxes. At first sight the logical sequence would appear to consist in placing the newest oxide in the last position in the gas stream and gradually fouling it by bringing it successively into earlier positions in the stream. In practice this is not always satisfactory because new oxide, particularly natural bog-ore, is not in the correct condition chemically or physically. In fact such oxide will frequently be found to give off traces of hydrogen sulphide when in contact with pure coal gas. The difficulty can be overcome by placing in the last box either a charge of oxide which has been once fouled and then revivified by contact with air or a mixture of revivified and new oxide. In the so-called backward-rotation system often adopted, a charge of oxide is placed first in contact with gas richest in hydrogen sulphide. When it has accumulated a high proportion of sulphide it will cease to absorb efficiently and is then transferred successively to the second position, relative to the gas inlet, where, owing to the low concentration of hydrogen sulphide, the regeneration reaction can become effective in reducing the sulphide content of the mass. The process of regeneration is completed in the third and fourth positions and the regenerated oxide then returned to the first position in contact with the foul gas. By adopting this cycle of operations, most of the hydrogen sulphide in the gas is retained in the early stages, while the sulphide mass is allowed to regenerate in its successive movements until, in the final position, it is in a suitable condition for the removal of the last traces of hydrogen sulphide from the gas.

The details given in Table VIII below show the results of observations made on the composition of a gas stream at various stages during its passage through purifiers worked on the backward rotation system. The figures are representative of the whole useful life of the charge in the box. The observations showed that in the first position the oxide would take out up to 95% of the hydrogen sulphide in the entering gas for a period which varied from 6 days on first fouling, down to 1 day when the oxide charge was nearly ready for discharging. These figures are given by H. Hollings and W. K. Hutchison (*l.c.*), who also analyse costs of the oxide purification process.

TABLE VIII.—REMOVAL OF HYDROGEN SULPHIDE IN OXIDE PURIFIERS.

	Hydrogen sulphide in gas.		
	Gr. per 100 cu. ft.	Parts per million.	O_2 in gas, % by volume.
Entering first box .	550	—	1·2
„ second box.	25	—	0·9
„ third box .	0·5	8·0	0·8
„ fourth box	0·01	0·17	0·7
Leaving fourth box .	0·001	0·017	0·7

A study of the costs of the gas purification process by means of oxide of iron is complicated by the fact that in any one year the quantities of new oxide bought and of spent oxide sold do not necessarily bear a proper relationship to the quantity and quality of the gas treated during that year. Table IX gives representative purification-costs for a modern system which includes elevation of the oxide to an overhead floor above the purifiers and provision for bottom discharge.

TABLE IX.—TYPICAL COSTS OF OXIDE PURIFICATION.

(Sulphur per million cu. ft. gas = 0·262 tons.)

	s. *d.*	*s.* *d.*	*d.*
Cost of new oxide :			
Per ton of new oxide .	29 2	—	—
per ton of sulphur . .	—	40 10	—
Cost of disposal of spent oxide :			
Per ton of spent oxide .	4 2	—	—
Per ton of sulphur . .	—	8 4	—
Total oxide charges :			
Per ton of sulphur . .	—	49 2	—
Per 1,000 cu. ft. of gas .	—	—	0·155
Process charges (moving oxide)	—	—	0·104
Supervision and maintenance of purifiers and buildings	—	—	0·082
Total operating charges. .	—	—	0·341
Credit for spent oxide :			
Per ton of sulphur . .	—	33 4	—
Per 1,000 cu. ft. of gas .	—	—	0·105
Net operating charges . .	—	—	0·236
Capital (8% on £5,100 per million cu. ft. per maximum day, 250 maximum days per year) . . .	—	-	0·392
			0·628

The use of towers in preference to the customary horizontal purification-boxes is being adopted in Germany and also in this country. The main objectives are minimum space requirements, minimum excavation, ease of operation and control, minimum labour in charging the purifying material in a single shift, minimum equipment and installation costs and minimum operating expense with even distribution of labour throughout the year. A description of a plant of this type has been given by C. M. Croft (Inst. Gas. Eng., Comm. No. 212, 1939).

Although a considerable amount of attention has been devoted with varying degrees of success to new methods of gas purification, using both wet and dry reagents, the oxide of iron method is still the method in general use. The high extraction efficiency required in this country is readily attainable at a cost which has defied attempts to supersede it. In other countries other purification processes are also in operation.

In the Koppers Iron Sulphur Process the gas is brought into contact with a suspension of iron hydroxide in sodium carbonate solution. The suspension is then subjected to the action of atomised air which revivifies the purifying medium and liberates free sulphur. In a modification of this process the iron hydroxide is replaced by a soluble nickel salt.

The Petit process of liquid purification uses potassium carbonate to remove hydrogen sulphide. In regenerating the fouled liquor, carbon dioxide is introduced whereby the hydrogen sulphide is expelled; bicarbonate is then converted to carbonate by heating, the carbon dioxide being recovered. The expelled hydrogen sulphide is absorbed in iron oxide from which the sulphur is recovered after revivification with air.

The removal of the organic sulphur-compounds from the gas presents much greater difficulties than does that of hydrogen sulphide. Considerable attention is now being devoted to the elimination of these organic compounds and recent researches have made possible a considerable reduction in the sulphur content due to these substances. Before discussing the matter in detail, however, it is desirable to consider the removal of naphthalene and of benzole from gas, with which latter operation the elimination of sulphur compounds is closely connected.

Naphthalene Removal.—Mention has already been made of the difficulty which can arise from blockages both in the plant and mains on the works and on the mains and services in the district of supply, from the deposition of solid naphthalene from the gas. In the early days of the industry, when lower carbonisation-temperatures were employed, no difficulty was experienced in this respect, as, although considerable amounts of naphthalene were even then present in the hot gas, the amount of other tar constituents boiling at the same or a lower temperature than naphthalene was sufficient to effect a practically complete washing-out of the naphthalene from the gas in the ordinary process of condensation. As carbonising temperatures increased, trouble from naphthalene became more and more noticeable, at first only where coals from the Durham coal-field were carbonised, but eventually, with still higher carbonising temperatures, from all classes of coal, and very serious nuisance from naphthalene stoppages took place, both manufacturers and consumers being affected.

The difficulty arises from the fact already discussed, that increased carbonising-temperatures, particularly when there is also a considerable free space above the coal in the retort, effect an increase in the production of naphthalene and a decrease in the production of lower-boiling tar oils. The proportion of the latter is then insufficient to effect the complete washing-out of the naphthalene from the gas at the cold end of the condenser, and the gas may, therefore, leave the latter almost saturated with naphthalene vapour at the temperature of the condenser outlet, such gas then becoming supersaturated on further cooling in the works or district of supply, and then under favourable conditions depositing solid naphthalene, mostly in the form of very bulky flaky crystals, a very small weight of which is capable of causing a serious blockage.

Two methods of treatment may be employed, the one consisting in washing the gas with suitable naphthalene solvents and the second in adding to the gas the vapours of certain liquids which dissolve naphthalene. The method normally employed in this country consists in scrubbing the gas with oil in a washer of the type used for ammonia recovery. The oil may be the creosote or green oil fraction of coal tar, boiling at 270–350°, or petroleum gas oil may be used. A number of other solvent oils have also received attention. The removal of naphthalene is frequently undertaken simultaneously with benzole extraction on those works at which the latter operation is carried out.

Extraction of Benzole.—The recovery of benzole which has long been practised by the coking industry, exerts a marked influence on production figures because it derives benzole not only from the by-product tar but also from the gas, which contains 20–30 times as much benzole per ton of coal as does the tar. So long as the gas industry on the other hand was selling on a luminosity basis, gas from this latter source could not be exploited for the production of benzole. The abnormal conditions caused by the war (1914–15), however, followed in 1920 by the removal of the restrictions on the illuminating power of the gas, created a different position. Even so, the relatively high value of benzole in gaseous form may still militate against its recovery, except under specially favourable conditions. These depend on a number of factors which have been considered in detail by H. Hollings (Trans. World Power Conference, 1930, 2, 63).

The recovery of benzole at gasworks by means of oil washing became general in this country during the war (1914–18) and reached a peak in 1917. At the end of the war production fell again but has recently increased as the result of the fiscal enactments, already described (p. 435), designed to encourage the production of spirit from indigenous materials. This policy has resulted in a considerable development of benzole extraction from gas on the gasworks, the quantity of spirit so produced being estimated at between 10 and 11 million gallons in 1934 (A. K. Steel, J. Inst. Petroleum Tech., 1935, 21, 450). The number of gas undertakings responsible for this production—some 20% of the country's total production—was then about 90.

Similar results from protective measures can be seen in other countries where a falling-off in imports is being accompanied by an increase in the quantity produced internally.

Benzole finds a ready sale as a motor fuel, for which purpose it has valuable properties. In addition some 30–40 million gallons per annum, or 15–20% of the world's production, is used for industrial purposes. The continued growth of the automobile industry should ensure a ready outlet for considerably larger quantities, as the present consumption forms only a small percentage of the total consumption of motor spirit. W. G. Adam and G. W. Anderson (Trans. Chem. Eng. Congr., World Power Conf. 1936, C 7) state that this percentage ranges from a minimum of 0·5% in the United States to a maximum of about 16% in Germany.

Reference is made in this section to those aspects of benzole production which have particular reference to its recovery from coal gas on the gas-works. Standard methods adopted for the recovery of crude benzole from coke oven gas by the coking industry are also employed by the gas industry (*v.* COKE MANUFACTURE AND RECOVERY OF BY-PRODUCTS).

The well-established method for the recovery of benzole from coal gas, known as the oil-washing process, has a number of definite advantages when considered from the viewpoint of the gas-works and, in fact, it was until recently the only method employed. The process consists essentially in scrubbing the gas in a washer containing gas oil or other suitable oil. The washing oil used, whether it be creosote oil or gas oil, is usually readily obtainable and there is a ready means of disposal of the spent oils in each case. The former can be run to the tar tanks, whilst the latter may be disposed of in the carburetted water-gas plant. Another advantage of the oil-washing process in comparison with the adsorption process described below is the comparative ease with which the removal of benzole may be combined with the removal of naphthalene. In fact the two operations can be carried out in a single washer. In many cases it is considered essential to install an oil washer for the removal of naphthalene, irrespective of whether benzole is removed or not. In such circumstances the process of benzole removal is obviously free from the capital charge in respect of the washer and has to bear only the capital charge of the oil circulation and distillation system.

It is desirable to use separate washers for naphthalene removal and benzole recovery, when complete freedom from naphthalene in the gas is desired. In such cases, if the naphthalene washer is placed after the benzole washer, advantage may be taken of the increase in absorptive capacity and reduction in viscosity of the wash-oil in the benzole scrubber, caused by the presence of naphthalene in solution in the oil (Report Benzole Research Committee, 1928, 151). The oil fed to the naphthalene washer should be quite free from naphthalene; this presents no difficulty if gas oil is used for carburetting in the water-gas plant. There appears to be no objection to the use of oil from the naphthalene scrubber for making up losses in the benzole scrubber, provided the same type of oil is used in both.

The type of washer used has an important bearing upon process efficiency. The multi-bay horizontal rotary washer is popular in the gas industry, because of its low back-pressure and ease of control but, as shown by L. Silver (Gas J., 1934, **205**, 372), it is unsuitable where a high extraction- and process-efficiency is desired, owing to the impossibility of maintaining the necessary high rate of circulation of the washing medium, which is of the order of 60–90 gallons of gas oil per 10,000 cu. ft. of gas. Its use is, therefore, limited to the partial extraction of benzole from gas. A washer free from this drawback is the multi-stage static washer, which consists essentially of a series of tower scrubbers and so possesses features similar to these. It approaches more closely to the ideal of counter-current flow and provides the required contact between gas and washing oil. Low initial cost and low back-pressure are additional advantages. The results of a comprehensive survey of the absorptive capacities of oils which have been used or proposed for benzole recovery are summarised by W. H. Hoffert and G. Claxton (Inst. Gas Eng. Comm. 1930, No. 8) in a discussion on benzole recovery with particular reference to gasworks practice.

The ability of certain specially prepared charcoals to adsorb gases and vapours has long been known, but it was not until recent years that this property has been utilised on a large scale for the extraction of benzole from coal gas (*v.* Vol. III, 271–276). In 1916 the Bayer Company of Germany patented (G.P. 310092) a benzole-recovery process employing activated charcoal. Since that date considerable interest has been displayed in this alternative method for the recovery of benzole and large-scale plant are now in operation. One of these installations, at the Beckton Works of the Gas Light and Coke Company, has a daily capacity of 70–75 million cu. ft. of coal gas and an output of 20,000 gallons of benzole. Operating efficiency is 92·5% (*cf.* H. Hollings and S. Hay, Chem. and Ind. 1934, **53**, 143).

The efficiency of the oil-washing process, which is still the more popular, has increased appreciably as the result of competition from the active-carbon process. The quality of the benzole produced, and also the consumption of steam, have improved so that the difference between the two processes is not now so marked as it was when the active-carbon process was first introduced. The production of benzole from coal gas has been comprehensively dealt with by W. H. Hoffert and G. Claxton ("Motor Benzole," National Benzole Association, 1938).

The quality of the crude benzole derived from coal gas depends largely upon the conditions of carbonisation (*cf.* W. A. Voss, J.S.C.I. 1930, **49**, 343T.). In general, when the products of carbonisation escape from the gas retort or oven without having been submitted to secondary thermal decomposition, the crude benzole recovered contains a relatively high proportion of paraffins and also of unsaturated hydrocarbons. For example, benzole from gas made in a lightly filled horizontal retort contains less unsaturated and paraffinic substances than does that recovered from gas made in continuously operated vertical retorts or in completely filled intermittently operated retorts.

REMOVAL OF ORGANIC SULPHUR-COMPOUNDS.—The increased efficiency of benzole extraction in the gas industry during recent years has had a marked effect upon the sulphur content of the gas distributed. Reduction of the organic sulphur content of town's gas to a minimum is desirable in many ways, notably in reducing corrosion of heating appliances, in enabling flueless heaters to be more generally used without nuisance from the odour of sulphur oxides, and in improving furnace atmospheres in the heat treatment and, more particularly, the bright annealing of metals. Several processes, whereby the sulphur content can be reduced to 10 grains per 100 cu. ft., have been tested in large-scale operation.

The process of the South Metropolitan Gas Company consists in passing the gas at 450° over a catalyst of nickel on porous fire-clay (*cf.* E. V. Evans, J.S.C.I. 1915, **34**, 9). Under these conditions the carbon disulphide reacts with hydrogen in the gas, yielding hydrogen sulphide and carbon,

$$CS_2+2H_2=2H_2S+C.$$

In carrying out the process the gas freed from hydrogen sulphide passes first through a tubular heat exchanger, where it is heated by the hot gas coming from the catalysing tubes, and thence to a heated chamber in which are assembled the vertical 6 in. tubes filled with the catalyst, maintained at 420–440°. The treated gas passes through the heat exchanger, giving up a large portion of its heat to the incoming cold gas, and thence, after cooling, to oxide of iron purifiers for the removal of the hydrogen sulphide. Apart from the conversion of the carbon disulphide and the decomposition of a small amount of hydrogen cyanide to ammonia, no material change takes place in the gas. The carbon deposited during the reaction accumulates on the catalyst and is periodically removed by burning under controlled conditions in a stream of air.

The active-carbon process removes about 75% of the total sulphur compounds. Methods for their separation from the benzole are given in detail by W. G. Adam and G. W. Anderson (*l.c.*).

The normal oil-washing process removes only about half the above quantity of sulphur. A modified method has, however, been described by W. K. Hutchison (Inst. Gas. Eng. 1937, Comm. No. 175; *cf.* B.P. 443094), whereby the sulphur content of the gas should be economically reducible to less than 10 grains per cu. ft. In this process more than the normal quantity of oil is circulated, but it is distilled under reduced pressure to minimise steam consumption.

A catalytic process for the removal of the organic sulphur-compounds which is capable of reducing the sulphur content to 4 grains per 100 cu. ft. is described by R. H. Griffith (Inst. Gas. Eng. 1937, Comm. No. 175). It is expected that gas treated by this catalytic process, followed by active-charcoal treatment for the recovery of benzole, will have a sulphur content which may be below 1 grain per 100 cu. ft. A catalyst consisting of nickel deposited on white china clay is employed. The catalyst used appears to differ in two respects from that employed in the South Metropolitan process. The latter was (*a*) prepared from nickel chloride by the action of coal gas at a high temperature without the intermediate production of the hydroxide, and (*b*) deposited on a different support material. No deposition of carbon on the catalyst takes place in the more recent process. The reaction is one of oxidation, the sulphur compounds undergoing catalytic oxidation to sulphur dioxide and carbon dioxide by combination with oxygen in the gas:

$$CS_2+3O_2=CO_2+2SO_2$$
$$2COS+3O_2=2CO_2+2SO_2$$

This process has the advantage of eliminating nitric oxide simultaneously, an important feature where trouble is experienced from nitrogenous gum formation in gas (*see* p. 468*a*).

SIMULTANEOUS REMOVAL OF HYDROGEN SULPHIDE, CARBON DIOXIDE AND CARBON DISULPHIDE BY MEANS OF LIME.—This old process consists in subjecting the gas to the action of calcium hydrosulphide formed by the action of hydrogen sulphide on lime. The calcium hydrosulphide absorbs so large a proportion of the carbon disulphide that the total amount of sulphur left in the gas can be reduced to 12–20 grains per 100 cu. ft. The objections to this process are as follows:

(1) The spent material consists of a mass containing calcium sulphide, having a smell of hydrogen sulphide, etc.

(2) The discharging of the spent material from the boxes is unpleasant to the men employed.

(3) The process is somewhat uncertain in action.

(4) Great difficulty is experienced in disposal of the spent material except in smaller undertakings in agricultural districts.

Apart from these objections, this method involves the complete removal of carbon dioxide whether this is advisable or not.

It has long been known that by re-heating the gas freed from hydrogen sulphide to 300–350° the carbon disulphide is largely converted into hydrogen sulphide, which may then be removed by oxide of iron purification, but practical difficulties in large-scale working prevented its adoption. (For a full account of these methods, *see* Carpenter, J. Gas Lighting, 1914, **126**, 928.) The first successful plant of any magnitude for carrying out the method was that of Hall and Papst at the Oregon Works, U.S.A., where a plant was erected dealing with 4,000,000 cu. ft. of gas per day, and effected an average reduction of the sulphur from 58 to 17 grains per 100 cu. ft.

REMOVAL AND RECOVERY OF CYANOGEN COMPOUNDS.—It has long been known that crude coal gas contains hydrogen cyanide and probably other cyanogen compounds. The total amount varies considerably at different works, but under the conditions of modern practice the amount of hydrogen cyanide in the gas leaving the retorts averages about 120–130 grains per 100 cu. ft. About one-quarter of this is removed in the virgin liquor during condensation, partly as ammonium cyanide, but chiefly as ammonium thiocyanate, into which the cyanide also passes on storage. Smaller amounts are similarly absorbed in the washers and scrubbers but, with high retort-temperatures, 90–100 grains per 100 cu. ft. (equivalent to 4–4·5 lb. of sodium ferrocyanide, $Na_4FeCy_6,10H_2O$, per ton of coal) usually remain in the gas entering the purifiers. This is absorbed by the oxide in the purifiers with formation of a number of compounds as the result of somewhat complicated reactions. The cyanogen compounds in the spent oxide occur normally as ferrous ferrocyanide, ferrous ammonium ferrocyanide, ferrous ammonium carbonyl ferrocyanide, ferropentacyanide, and also as thiocyanates of ammonium, iron, and calcium. The ferrocyanides are classified together as Prussian Blue and vary in amount from

1% to 9% in a spent oxide containing 50% of sulphur. The thiocyanates may be present in amounts which vary, in general, from nil to 7%.

It is a fortunate fact that conditions in the purifier which favour the satisfactory removal of hydrogen sulphide also favour the removal of hydrogen cyanide. It should be noted, however, that hydrogen cyanide is absorbed and fixed only by ferrous oxide or iron sulphides. In other words it is not absorbed by fresh or fully revivified oxide. The maintenance of satisfactory conditions in the purifiers has been fully discussed by R. H. Clayton, H. E. Williams and H. B. Avery (Gas J., 1931, **196**, 311), particularly with regard to moisture, oxygen and ammonia control. The formation of large amounts of ammonium salts gives rise to undesirable conditions and should be avoided. It is important in this respect that the sulphided layer should be deep, thereby favouring the formation of Blue and not thiocyanate. Excessive quantities of ammonia in the gas are to be guarded against for the same reason.

Hydrogen cyanide can be completely absorbed by lime purification.

Other Purification Processes.—As already mentioned, a portion of the hydrogen sulphide is removed with the ammonia, being absorbed by the aqueous ammoniacal solution with formation of ammonium sulphides, but the amount of ammonia present is much below that required for complete removal. Many attempts have been made to modify the scrubbing process in such a way as to effect simultaneous removal of sulphur impurities and, in some cases, of the carbon dioxide as well. Hills (B.P. 1369, 1868; 934, 1874; 1895, 1875) based a process on the fact that when ammonia liquor is heated to about 90° it gives off large quantities of hydrogen sulphide and carbon dioxide, but only very small quantities of ammonia, the residual liquor then containing large amounts of free ammonia, available for washing further quantities of gas. Claus (B.P. 2838 and 2865, 1881; 4644, 1882; 5959, 1883) combined Hill's process with the continuous distillation of a large amount of the liquor, the ammonia being returned to the gas, so that the amount of ammonia in the gas in the scrubbers was four or five times that normally present. By washing, in addition, with a solution of ammonium polysulphide, the amounts of hydrogen cyanide and carbon disulphide were largely reduced. The hydrogen sulphide was converted to sulphur and recovered. Considerable losses of ammonia, and other difficulties operated against the success of the process.

Attempts along these lines continue, and while some of the processes evolved have been considered sufficiently satisfactory to justify large-scale operation, there is, as yet, no evidence that conventional methods embodying separate removal of the sulphur compounds have been seriously challenged. It is not possible to enumerate all the methods proposed, but one or two examples may be given. The Rostin process consists in mixing the gas in a washer with ammonia liquor which has been passed over copper oxide. The resulting copper sulphide is filtered off and the copper recovered as oxide. The liquor, after use, is returned to the vessel containing the granular oxide, where it is recharged and becomes ready for use again. The gas, thus freed from hydrogen sulphide, is then passed at 150° through a tower charged with a special ore for the removal of organic sulphur compounds. An experimental plant embodying this process is described by A. Thau (Glückauf, 1935, **75**, 541). A process installed at Billingham is described by F. F. Smith and O. R. Pryde (Chem. and Ind. 1934, 657). This depends on the reduction and oxidation of ammonium ferrocyanide and utilises the ammonia in the gas as the alkali in the scrubbing solution. Simultaneous removal of the hydrogen sulphide, the hydrogen cyanide and about 60% of the ammonia takes place. Apparently most of the ammonia is lost into the atmosphere; 80% of the sulphur is recovered.

Various methods have been proposed for the recovery of the ammonia directly as sulphate, by utilising the hydrogen sulphide as a source of the sulphuric acid. Such methods include those of Burkheiser (B.P. 20920, 21763, 1908; 17359, 1910; 16172, 1912) and of Feld (B.P. 3061, 1909; 5838, 1911; 157, 10147, 1912; Z. angew Chem. 1912, **25**, 705). H. Baar (Brennstoff-Chem. 1937, **18**, 248) has described a process for the simultaneous removal of ammonia and hydrogen sulphide by which the crude gas, after the addition of air, is oxidised catalytically at 350–450° and the sulphur dioxide extracted by the ammonia in the gas. The sulphite formed is oxidised to sulphate. Numerous other processes along these lines are described in the literature.

Gas Drying.—Water present in the gas entering a distribution system is responsible for corrosion with its subsequent expense in the upkeep of mains, pipes, meters and appliances. Accumulation of water will lead also to blockages. It is with the object of overcoming these and other drawbacks that attention has been directed to the dehydration of gas, a subject which is rapidly assuming importance in the gas industry.

Water vapour may be removed from the gas by several means, viz.: by compression, by refrigeration, by the use of solid adsorbents or of hygroscopic substances, either solid or liquid, and processes for the dehydration of gas based on these have been evolved.

Most of the methods actually in operation are based on the use of a hygroscopic solution, the most commonly used being calcium chloride.

A typical gas dehydration plant consists of a tower scrubber with wood filling, down which is sprayed, counter-current, a 40% solution of calcium chloride. The solution, in passing to the tower, is cooled while a portion of the weakened solution, returning to the stock tank, is passed over an evaporator.

The position of the gas drying plant on the works is immediately before or immediately after the holder.

When naphthalene is deposited by cooling either wet or dry gas, the concentration retained by the gas at a given temperature is independent of the humidity of the gas. Whilst it may be deduced that dehydrated gas will more easily cause the evaporation of an old naphthalene deposit than will wet gas, it does not follow that on reaching a zone of lower temperature the dehydrated gas will be less liable to deposit solid naphthalene.

Gum Formation in Gas.—It has been a matter of general experience that there has been a marked decrease during recent years in the number of stoppages of service pipes and appliances, due to naphthalene, water and rust. Within the past few years, however, deposits of gummy material have been observed in appliances in certain areas. The complaints to which these gum deposits have given rise are less numerous than those formerly resulting from naphthalene, but where they occur the matter becomes an urgent one since it is found that the gum is most likely to create a nuisance in some of the most modern type of appliances. Pilot lights, fine adjustment valves and governors are the most sensitive units.

The gum deposited from town's gas in this country differs from the so-called *liquid phase gum* derived from rich carburetted water gas. It is characterised by a higher nitrogen content and is formed by the interaction of small quantities of nitric oxide, oxygen and unsaturated hydrocarbons, such as butadiene and *cyclo*pentadiene (*cf.* H. Hollings, Inst. Gas Eng. 1936, Comm. 147). All coal gas as manufactured under normal conditions in any type of retort, and all carburetted water gas, contain more than sufficient unsaturated hydrocarbons to react with all the nitric oxide present. When the benzole has been removed from the gas by active carbon, the diolefins may be removed to such an extent that reaction in the stripped gas is sluggish or suspended. In such cases the admixture of unstripped water gas is desirable to hasten gum precipitation. The normal type of oil washing process for benzole usually leaves sufficient diolefins in the gas for subsequent reaction to proceed normally. The concentration of nitric oxide in the gas is the important factor which determines whether or not gum formation is to be anticipated. Any concentration of nitric oxide in excess of 0·05 part per million of gas by volume may give rise to trouble. Most of the nitric oxide in coal gas is due to waste combustion gases drawn into the retorts from the heating flues, or to air drawn in at the retort mouthpieces and burnt inside the retorts. Little nitric oxide is removed during the ammonia recovery process, but the oxide of iron purifiers normally absorb about 50% of it. The gas leaving the purifiers contains nitric oxide but no gum. Most of the gum is formed in the gasholders, although any nitric oxide in the gas leaving the works may react later to form gum during distribution. Gas-holders, therefore have two functions in addition to storage:

(1) To allow time for any nitric oxide in the gas to react, and

(2) To allow time for the gum formed to settle.

Gum particles settle at a greatly increased rate if there is simultaneous condensation of moisture, and it may even be necessary to add steam at the holder inlet in hot weather in order to promote saturation and subsequent condensation. Any gas drying process should be installed at the outlet of the gas-holders. The rate of reaction in coal gas between nitric oxide, oxygen and diolefins is primarily dependent upon the concentration of the diolefins and the reaction is often preceded by an induction period dependent on concentration and temperature. The distribution of a mixture of stored and unstored gas is objectionable because the reacting gas from the storage system may start a reaction in the unstored gas which would otherwise be inhibited by contact with the surfaces of the pipes.

Hydrogen Sulphide Contamination During Storage.—The phenomenon of hydrogen sulphide generation in gas-holder water was first described by Ymonet (J. de l'Éclairage au Gaz, 1898; J. Gas Lighting, 1898, **73**, 77; 1899, **74**, 370). In 1904 Tapley showed that bacterial reduction could bring about the formation of hydrogen sulphide from sulphates under conditions similar to those in holder tanks. The trouble appears to have become more frequent in recent years, and Evans (Gas World, 1932, **97**, 431) has pointed out that prior to the general adoption of naphthalene removal, solid naphthalene and associated heavy oils collected in holder tanks and saturated the water which was thereby rendered bactericidal.

During the autumn, atmospheric temperature changes can give rise to convection currents in the holder water, with the result that if bacterial action has been taking place in the water at the bottom this foul water rises to the surface. Many holders at this period begin to give off excessive quantities of hydrogen sulphide, and unless tests have been made in preceding months there will be little or no warning of the approach of quite high concentrations. The rapid reduction of sulphates is not confined to the holders, but is found in an exceptional degree in holders recently filled with pure town's or well water. The use of water with a low sulphate content is an obvious precaution. When the gas is being contaminated to an excessive degree it is necessary to consider steps for the removal of the hydrogen sulphide from the water; oxidation by means of aeration has proved efficient, but is liable to be objectionable, and the use of a regulated amount of hydrogen peroxide is to be preferred. Details of these and other methods are given in a combined report on the subject to the Institution of Gas Engineers by the Gas Light and Coke Company and the South Metropolitan Gas Company (Gas J. 1935, **212**, 505).

Yield of Gas and By-Products.—The volume of gas obtained varies according to the quality of the coal carbonised and to the conditions of carbonisation. The volume produced per ton of coal, without steaming the retorts, measured moist at 60°F. and 30 in. bar., usually falls within the limits of 9,000 and 14,000 cu. ft. From the same coal the higher the yield of gas the lower is the calorific value.

The chief constituents of purified coal gas, obtained by the simple carbonisation of coal, are: Hydrogen, Methane, Carbon Monoxide, Benzene, Ethylene, Nitrogen, Oxygen and Carbon Dioxide. Other substances are present in small quantity. The relative proportions naturally vary, but, for the most part, the chief constituents fall within the following limits:

	Per cent.
Hydrogen	38–55
Carbon Monoxide	4–15
Methane	22–25
Ethylene	2–4
Benzene	0·5–1
Oxygen	0–1·5
Carbon Dioxide	0–3
Nitrogen	2–20

A method for the assessment of gas-making results has been evolved by S. Pexton (J. Inst. Fuel, 1935, **8**, 200). It introduces a new term, "the hydrocarbon enrichment value," which may be expressed algebraically as follows:

$$E=\frac{V}{100{,}000}\left[H-318\left(1-\frac{N}{100}\right)\right]$$

where E=the hydrocarbon enrichment value, V=volume yield of purified gas per ton of coal or per gallon of gas oil, H=calorific value of the purified gas, and N=percentage of inerts in the purified gas. The simplicity of application and usefulness of the hydrocarbon enrichment value are due to the fact that, for given conditions, it is a single number depending solely on the yield and calorific value of the hydrocarbons themselves. The production of blue water-gas by steaming does not in any way complicate the employment of this index to show the enriching value of the hydrocarbons in the coal gas. In the absence of gas leakage from the retorts, the hydrocarbon enrichment value becomes an index of cracking conditions within the retort.

The yield of coal tar with horizontal retorts varies commonly from 9 to 13 gallons per ton of coal, averaging about 10 gallons, or some 5·5% of the weight of the original coal. Its sp.gr. varies from about 1·10 to 1·25, this depending largely upon the temperature of carbonisation. The higher the temperature to which the volatile products are exposed, the higher is the average carbon percentage and the lower the hydrogen percentage of the tar, and the greater the amount of the so-called "free carbon" formed; the latter, although in appearance resembling amorphous carbon, always contains hydrogen, and consists of derivatives of very complex hydrocarbons, which are infusible and insoluble in the remaining tar. The yield of tar from vertical retorts is higher and is increased by steaming, the tar being thinner and having a sp.gr. of 1·07–1·13. It contains only 40–55% of pitch instead of the 60–70% in tar from horizontal retorts, and also only small amounts of "free carbon."

The ammoniacal liquor contains a quantity of ammonia calculated as sulphate, equivalent generally to a yield of from 22 to 30 lb. of the latter per ton of coal. It is usually higher (up to 45 lb.) in continuous vertical-retorts, and is considerably increased by steaming. For the composition of ammoniacal liquor and its working up into ammonium salts, *v.* AMMONIA, Vol. I, p. 346.

The yield of coke averages about 14 cwt. per ton of coal, but some of this is used for heating the retort setting and for other purposes on the works, so that the amount available for sale is less than this, and a sale of 10 cwt. per ton is not often exceeded.

Manufacture of Carburetted Water Gas.

The reasons for the development of the carburetted water gas plant as a supplement to coal gas plant may be stated as follows:

(1) The chief raw material required is coke, which is a by-product from the carbonisation plant; the manufacture of a certain proportion of water gas therefore enables the gas undertaking to exercise some control over the coke market and to prevent the prices of coke being unduly depressed. Any fall in the price of coke increases the net cost of coal-gas manufacture, so that the water-gas plant plays an important part in stabilising the price of town's gas at a lower level.

(2) Because of the large variations which occur in the demand for gas at different seasons of the year, it is necessary to maintain a relatively large reserve of plant capacity capable of being brought into action at short notice. Water-gas plant is particularly suitable for meeting temporary and sudden demands for gas, not only because the capital charge involved when it is lying idle is less than the capital charge upon carbonising plant, but also because it can be brought into action at much shorter notice than can carbonising plant.

(3) The labour required for the manufacture of water gas is less than that required for the manufacturing of coal gas. This is a most important consideration in respect of any manufacturing unit, but is especially important in respect of a unit which may be required to work at irregular intervals.

One of the disabilities of the manufacture of water gas is that its calorific value is considerably less than that of coal gas and less than is generally considered desirable in a gas to be distributed for general use. Therefore, unless it is to be used in small proportions only, it is necessary to enrich it by means of oil from foreign sources of supply.

It will be appreciated that, since it is necessary that the mixture of coal gas and water gas should have a constant calorific value, it is necessary to use varying quantities of oil to produce varying quantities of carburetted water-gas if the output of the plant is to be varied from time to time, as it is in practice for the reasons given above.

The manufacture of water gas itself (commonly known as "blue" water gas, owing to its burning with a blue non-luminous flame) is dealt with in a separate article (*see* GAS, WATER), and will be considered here only so far as it concerns the manufacture of the carburetted gas. Fig. 21 illustrates the operation of a carburetted water-gas plant. Modern practice has added to this a number of refinements, which are described and illustrated below. These refinements do not affect the principles underlying the process, which can be more readily appreciated from this diagram of an early plant. The generator, A, is filled with coke, the latter being ignited at the bottom and raised to incandescence by blowing in air from a fan, the amount of air being regulated so that the gases coming away from the generator contain sufficient carbon monoxide to burn readily. These pass to the top of the "carburettor," F, which is filled with fire brick checker work, a secondary stream of air being added to the gas at the top when the carbon monoxide burns and raises the fire brick checker work to a red heat. The gases pass away from the bottom and enter the bottom of the "superheater," G, where they meet with more air, and the remaining carbon monoxide burns to the dioxide and raises the checker work in the superheater also to a red heat. Until recent years the waste gases were allowed to escape into the air from the "stack valve" on the top of the superheater, which is open during this operation. These gases pass away at a temperature ot 700° and the total of their potential and sensible heat content accounts for 20% of the heat contained in the coke consumed during the heating (blowing) and gas-making periods. The attachment of waste-heat boilers to water gas plant to recover this heat as steam has now become standard practice.

When the coke in the generator is sufficiently hot, and the checker work in the carburettor and superheater raised to the required temperature, all three air valves and the stack valve are closed and steam turned on to the generator, water gas being produced, which passes to the top of the carburettor. At this point oil is sprayed into the gas, and passes with the latter over the hot checker work, where it is volatilised, the vapours then undergoing decomposition, which is completed on passing through the superheater, the oil being thus converted into permanent gas and condensible tar vapours. The stack valve being now closed, the mixed gas passes through a seal pot, H, which prevents gas returning up the stand-pipe when the stack valve is open, thence through scrubbers filled with boards and tubular water-cooled condensers to reduce the gas to atmospheric temperature and condense the tar vapours and excess of steam from the gas. As the formation of water gas takes place with absorption of heat, the temperature of coke in the generator steadily falls, and eventually reaches a point at which the amount of carbon dioxide produced becomes excessive. The steam is then shut off, the oil having also been shut off from the carburettor a short time previously; the generator air-valve is then again opened and also the secondary air-valves and stack valve, and the coke and checker work raised to a suitable temperature as before, this period of working being known as the "blow." The gas-making cycle then recommences. From time to time steam is passed downwards instead of upwards through the generator during the run in order to control the distribution of temperature.

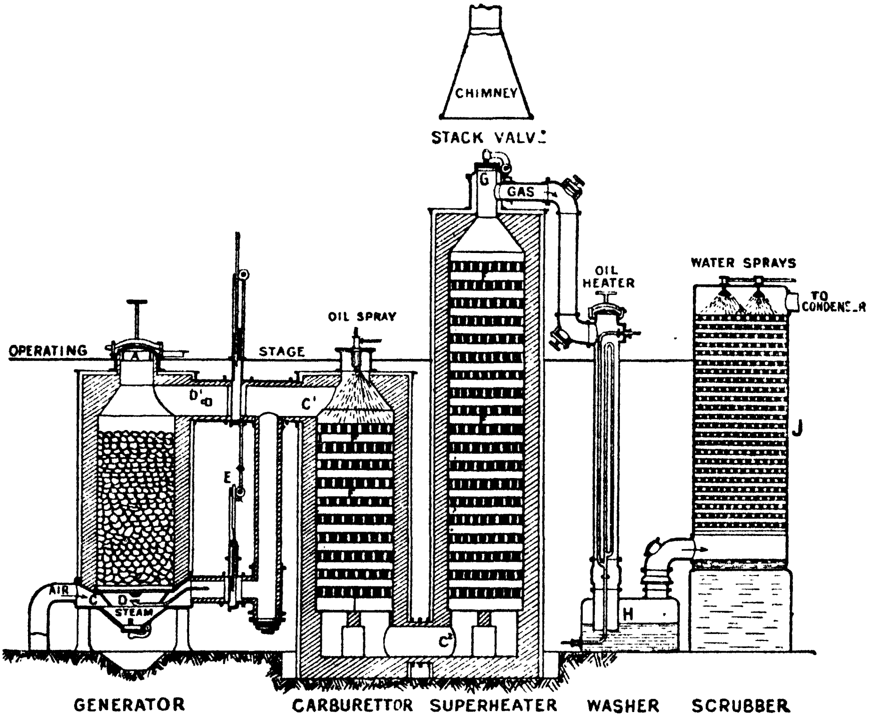


FIG. 21.—CARBURETTED WATER-GAS PLANT.

Several important advances have been made in the method of operation as exemplified in the plant just described, and a number of mechanical devices have been introduced. The use of the waste-heat boiler, already referred to, makes possible the generation of steam equivalent to 1¼–2¼ lb. per lb. of coke consumed in the generator or from 50 to 90 lb. per 1,000 cu. ft. of gas made. The steam requirements of carburetted water-gas plant for all purposes, including process steam, power for air blowers, gas exhausters, pumps, etc., average 80–100 lb. per 1,000 cu. ft. of gas. It will be apparent, therefore, that the application of waste-heat boilers results in the installation becoming practically self-supporting in the matter of steam supply. A modern plant is shown in Fig. 22.

Other improvements have led in the direction of reducing the arduous labour of removing the resulting clinkered ash. Automatic mechanical grates are now in use and are most successful when used with water-jacketed steel-walled generators. The upper part of such a generator is a steel shell lined with refractory material as in the older type of generator. The lower portion is a steel annular steam-boiler, which is used to prevent the adherence of clinker to the sides of the generator. The grate is conical in shape and is pierced for the passage of air, steam and gas. It is mounted on a steel drum which is attached to the ash pan. This pan is supported and kept in position by rollers and made to revolve slowly by means of a motor. In relation to the annular boiler the ash-pan revolves concentrically while the grates rotate eccentrically, the effect being to crush the clinker against a crushing plate. The broken clinker and ashes fall to the bottom of the pan and are extracted by a plough, a scraper placed diametrically opposite preventing the ash from consolidating on the bottom of the ash pan.

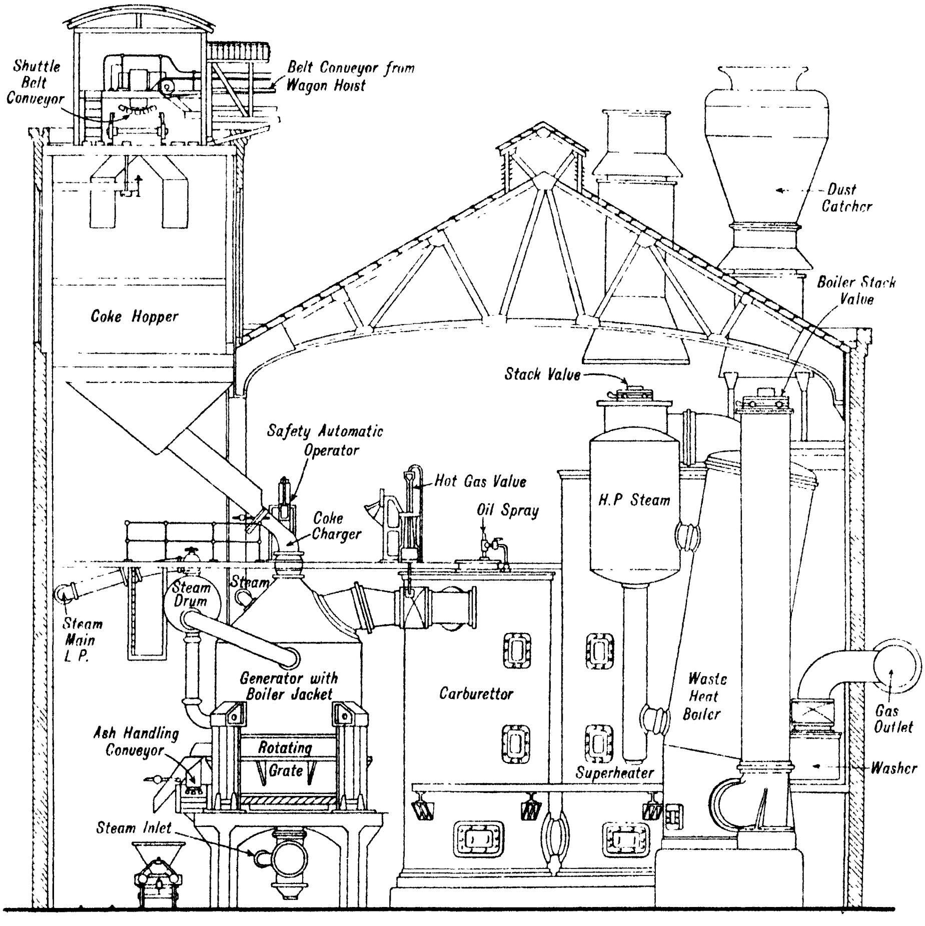


FIG. 22.—MODERN CARBURETTED WATER-GAS PLANT.

The time ordinarily occupied in clinkering is profitably employed in gas making. It is claimed that a boiler generator and rotary grate give a 10% increase in output over and above that obtained from a fixed-grate generator.

Automatic operators are now used to operate all the working valves of carburetted water-gas plant in safe and proper sequence at any desired intervals. Should any of the valves fail to operate or tend to operate in incorrect sequence, a safety device returns them all to the shut position, opens the stack, stops the auto-operator and gives audible warning.

THE BACK-RUN PROCESS.—The back-run itself is simply a " down-run " during which steam is admitted at the top of the superheater, passes downwards through the " superheater," upward through the carburettor and into the top of the generator. The blue gas made during the back-run is taken away through the cooling grate.

The following are details of a complete water-gas cycle, using the back-run process, and indicating the modern practice of using a rather short cycle.

Run.	Min.	Sec.
Up-run	1	30
Back-run	1	0
Purge (up)	0	10
Total run	2	40
Blow	1	50
Complete cycle	4	30

Oil is admitted during the up-run only. It should be realised that with the use of the back-run less heat is available for recovery in waste-heat boilers.

The introduction of waste-heat boilers, rotary self-cleaning grates, the back-run process and automatic operation have resulted in considerably lowering working costs with greatly increased outputs per unit. The efficiency of water-gas manufacture itself is not so high as that of the carbonisation of coal. Without oil enrichment or waste-heat recovery the thermal efficiency is 46–50%. The addition of waste-heat boilers raises this to 60% and the high efficiency of oil cracking gives an efficiency of 70% for carburetted water-gas manufacture under modern conditions.

The oil employed is mostly that fraction of petroleum lying between the burning oils (kerosene) and the lubricating oils, and is referred to as " gas oil." The amount of oil used depends upon the required calorific value of the carburetted water-gas. Each gallon used per 1,000 cu. ft. raises the calorific value by very approximately 100 B.Th.U. The practice of pre-heating the gas oil is less in favour now than formerly, since it gives rise to a number of practical difficulties. Recent American practice includes the use of butane for enrichment (*cf.* W. K. Beard, Proc. Amer. Gas. Assoc. 1935, 753). Investigation has shown the importance of a knowledge of the oil-cracking process, notably in relation to the nature of the gas oil, the temperature of cracking and the rate at which the oil vapours pass through the cracking zone. Laboratory and full-scale work on the subject is described in detail by R. H. Griffith (" The Manufacture of Gas : Water Gas," Benn, 1934).

As the gas production is intermittent, a balancing reservoir is required for the gas if this is to be passed through the purifiers at a uniform rate. For this purpose a relief gas-holder is placed at the condenser outlet into which the gas passes intermittently as made, and is drawn from it continuously by an exhauster and forced forward to the purifiers. The gas is purified from tar fog and hydrogen sulphide by the same methods as adopted with coal gas. Usually separate purifiers are employed for this gas, the purified streams of coal gas and carburetted water-gas mixing together at the outlet of their respective meters before reaching the holders.

The only by-product obtained other than spent oxide from the purifiers is the oil tar, no ammonia being produced in the process. The oil tar is a comparatively thin oil of sp.gr. 1·0–1·05, consisting mainly of aromatic hydrocarbons. It contains only about 30–35% of pitch and scarcely any " free carbon," the solid matter found in it consisting chiefly of fine coke ash carried over from the generator with the stream of water gas.

The amount of coke employed in the manufacture, including that used for raising steam, has fallen steadily with technical development. The figure for all authorised undertakings in this country was 44·5 lb. per 1,000 cu. ft. of gas made in 1936, as compared with 55·9 lb. per 1,000 cu. ft. in 1921.

The following is an analysis of a typical carburetted water gas having a calorific value of 450 B.Th.U. per cu. ft. :

CO_2	5·9
O_2	0·4
C_nH_m	7·0
CO	32·2
H_2	37·8
CH_4	9·1
C_2H_6	2·2
N_2	5·4
	100.0

As explained already gases of higher or lower calorific value may be produced by using more or less oil, the gases then contain a greater or less percentage of hydrocarbons.

COMPLETE GASSIFICATION.—Many attempts have been made from time to time to devise apparatus for the complete gasification of raw coal in a single stage, *i.e.* to give various mixtures of coal gas, water gas and producer gas, leaving a residue of clinker. The use of coal in the water-gas generator forms the basis of a number of these processes. No process has yet proved to be generally acceptable to the gas industry, although there is considerable interest in investigations which are in progress in various quarters. It should perhaps be pointed out that the adoption of any of these processes on a large scale would have a profound effect upon the relationship of the industry to the coke market. In connection with some of the processes consideration might have to be given to the high carbon monoxide content of the gas and to a decrease in the calorific value of the gas supplied. The latter consideration raises serious economic questions relative to the capacity of storage and distribution systems. Such processes are attractive, however, because they open up a possibility of a much more general substitution of gaseous for solid fuel in domestic life. It is not possible to describe the various processes in detail here, but reference may be made to the Doppel-Gas plant of Strache (J. für Gasbel., 1920, **63**, 230, 399) and the Pier process of Murdock, Evans and Lungren (Amer. Gas Assoc. 1925). H. J.

Hodsman and J. W. Cobb (Trans. Inst. Gas Eng., 1919–20, 429) drew attention to the advantages to be derived from the use of oxygen in the gasification of solid fuel. In the Lurgi process (Inst. Gas Eng. 1936, Comm. No. 141, 13) the gasification of brown coal is carried out by means of steam and oxygen under a pressure of about 20 atm. Working under the auspices of the Institution of Gas Engineers at Leeds University, F. Dent (*ibid.* 1936, Comm. No. 141; *cf. also* E. V. Evans, *ibid.* 1938, Comm. No. 180), has gasified fuels at pressures up to 50 atm. and has shown that under suitable conditions large quantities of methane may be formed.

Measurement, Storage and Distribution.

The gas leaving the purifiers passes to the station meters, in which its volume is measured, and thence to the gas-holders, where it is stored ready for distribution as required. The meters employed are usually wet meters, similar to those used as consumers' meters but considerably larger. To save ground space and initial cost, use is being made to an increasing extent of the Connersville meter (Fig. 23), which is an accurately constructed inverted Roots blower with two egg-shaped rotors; of the shunt meter, wherein a small meter registers the volume of a proportion diverted through a shunt as is normally done in electrical practice; and of meters which function by measuring heat supplied as electricity to warm the passing gas through a small and defined temperature range of about 4°F.

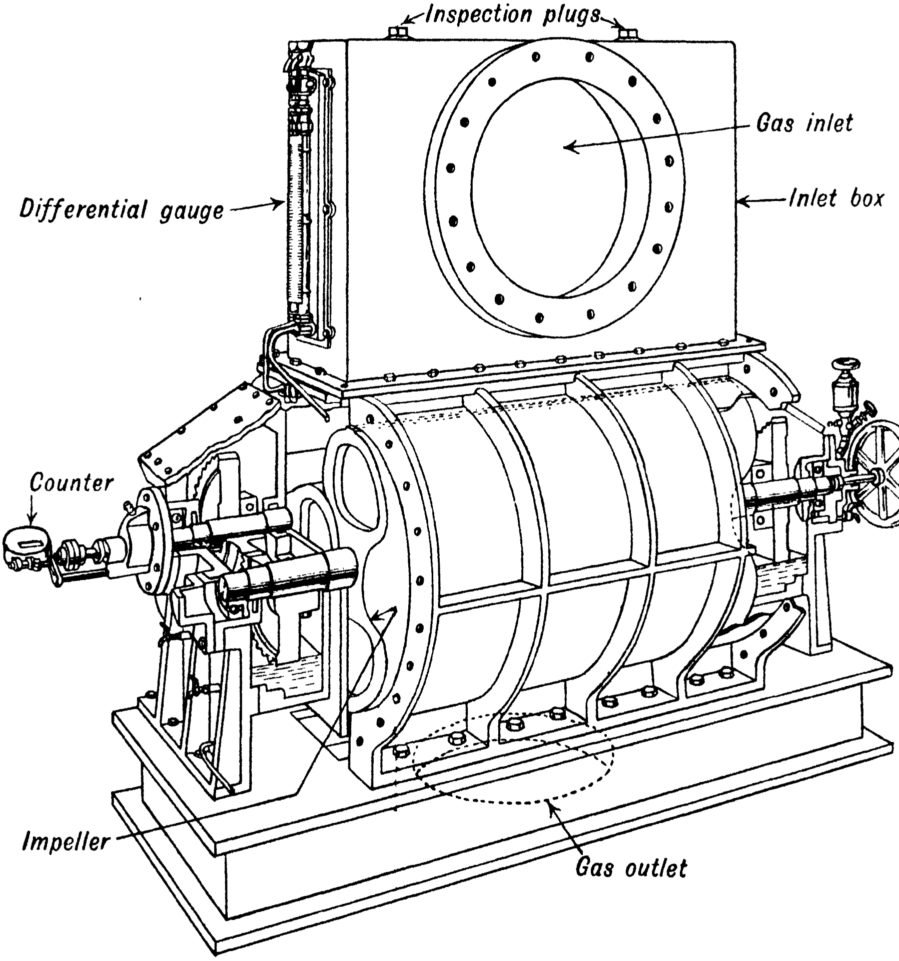
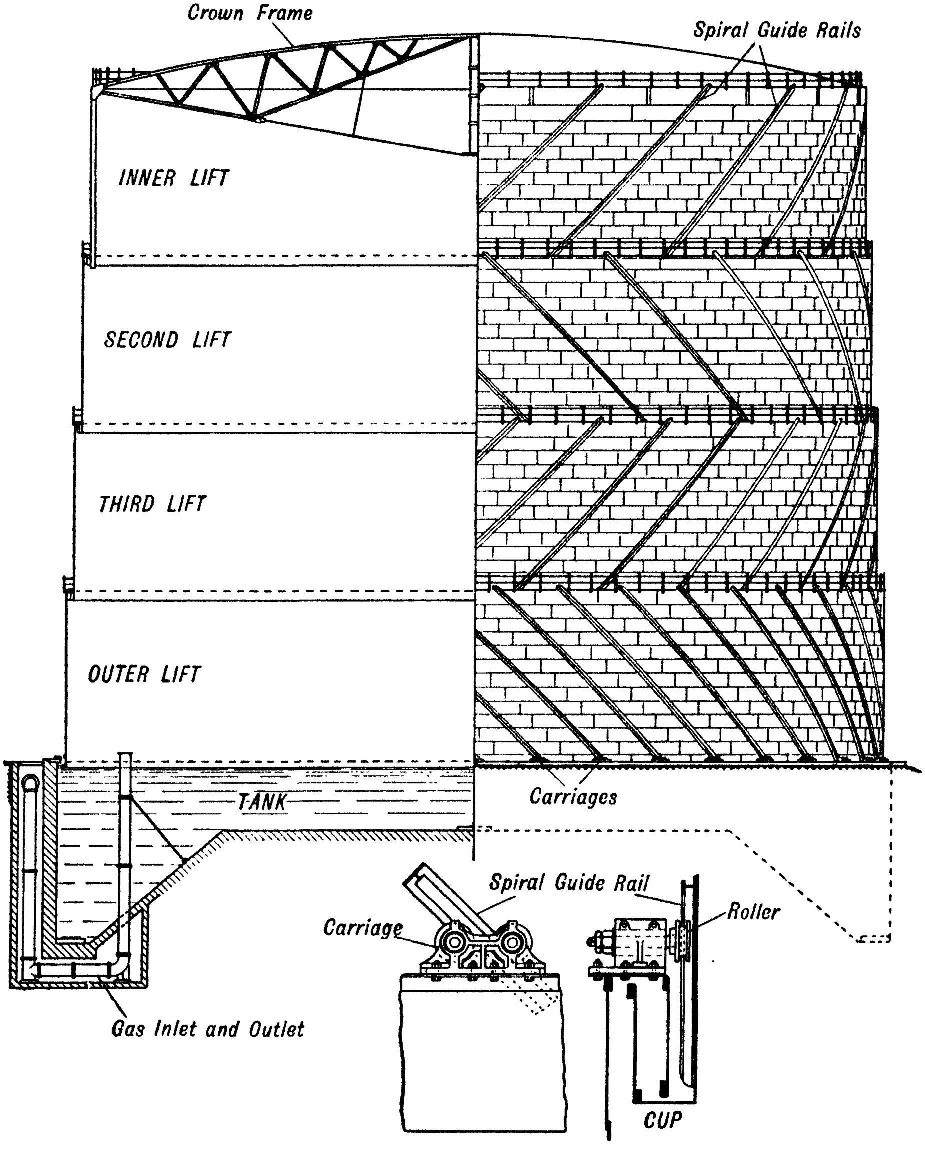


Fig. 23.—Connersville Meter.

The volume recorded by the meter is corrected to a standard temperature and pressure, the standard adopted throughout the industry being gas at 60°F. and 30 in. bar., saturated with moisture.

The type of gas-holder most largely used consists essentially of a large inverted bell in a tank of water (Fig. 24). In order to reduce the necessary depth of the tank, the bell is usually constructed in a number of lifts which slide into each other in a manner somewhat similar to the sections of a telescope. The guide framing surrounding it is of all-steel construction. In bell holders of the spiral guided type, which are also very common, a guide framing is dispensed with and inclined rails attached to the sides of the lifts cause them to rise after the manner of a screw thread and lock them in a rigid structure when inflated. All telescopic holders throw a varying pressure according to the degree of inflation.

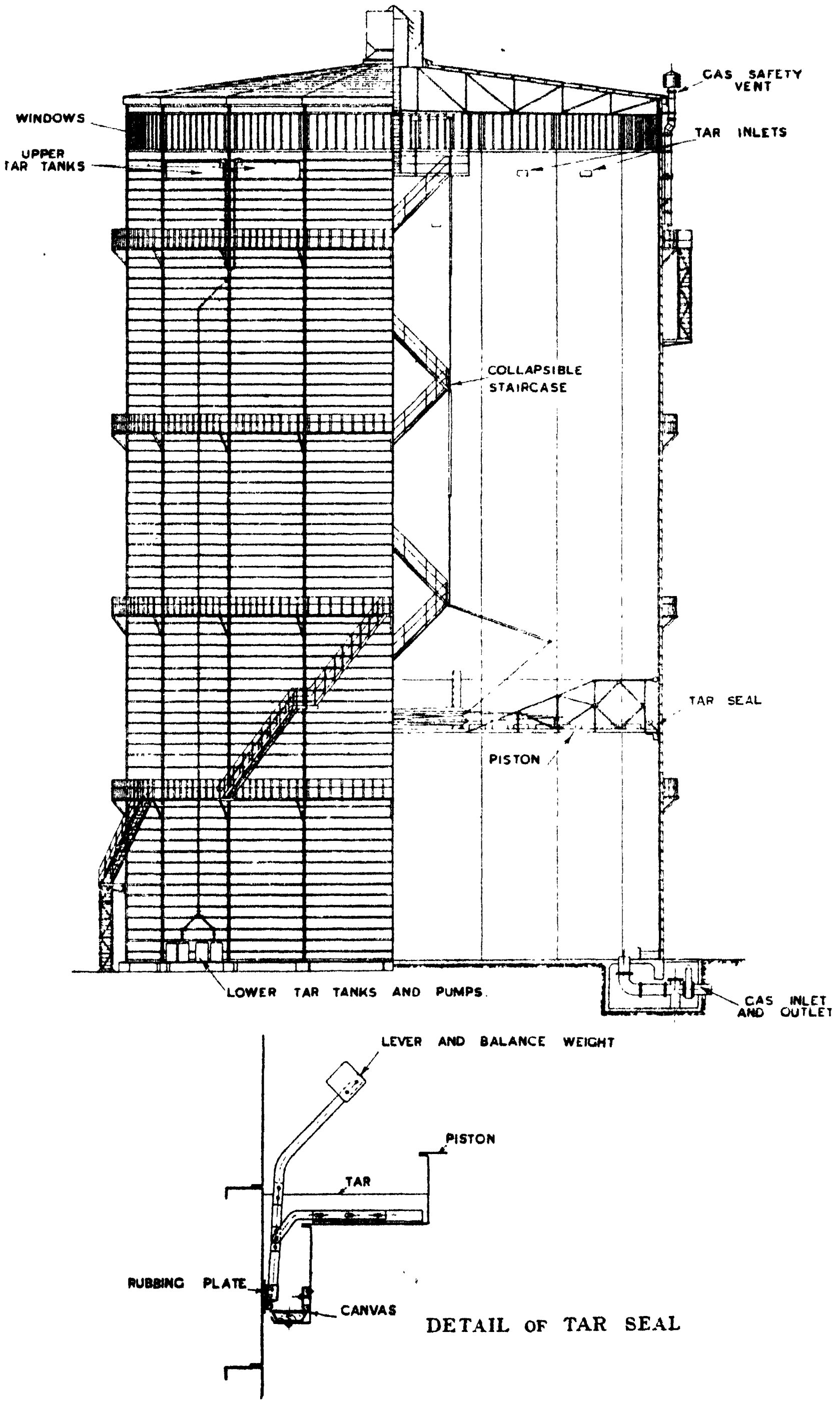


Detail of Spiral Guide Carriages

FIG. 24.—SECTION THROUGH GAS-HOLDER AND TANK.

Normal figures would be 3-in. water gauge for the inner bell, plus 2-in. water gauge for each succeeding lift. Thus a four-lift holder might give 3-in. pressure when completely uncupped and 9-in. when full.

A considerable number of holders recently constructed have been of the waterless type. Within a circular or polygonal vertical cylinder



DETAIL OF TAR SEAL

Fig. 25.—Waterless Holder.

of fixed dimensions a horizontal piston rises and falls, being at the base when the holder is empty and at the top when it is full.

The piston is sealed around its edge against gas leakage:

(*a*) By a tar seal kept filled by an automatic pump.
(*b*) By a flexible packing ring of rubber cotton fabric lightly greased, or
(*c*) By a hollow leather ring filled with oil under slight pressure which exudes through the leather and provides lubrication.

Examples of the first and second types are to be found in various countries of the world, and Fig. 25 gives a section of type (*a*) the most generally adopted. Larger capacities can be provided by waterless holders, which are built to hold up to 20 million cu. ft. These holders have the following advantages:

(*a*) The pressure thrown, which by weighting the piston can be up to 15 in. w.g., is practically uniform whatever the state of inflation.
(*b*) The gas is stored out of contact with water.
(*c*) The absence of the water tank reduces considerably the weight on the foundations.
(*d*) All parts needing adjustment can be attended to whilst the holder is in use.

In order to control the pressure of the gas in the mains in the district of supply, a governor is fixed between the holder and the trunk mains, whereby the pressure in the distribution mains is reduced to that most suitable. Fig. 26 gives a section of a governor. The gas, entering in the direction shown by the arrows, must, in order to reach the outlet, pass through a device consisting of a hollow vertical cylinder closed at the top and having a number of slots cut in the vertical side, the width of which increase towards the top of the cylinder. The top of this cylinder is connected by a rod to the bell above, and is capable of moving freely up and down with this bell which is sealed in water. When water is allowed to run into the annular chamber in the bell, the latter increases in weight, and with the attached cylindrical device sinks, increasing the size of the openings through which the gas can pass, and by adjustment of the amount of water the desired pressure at the outlet can be obtained. If, then, owing to increased consumption, the pressure of the gas in the outlet main falls, this lessened pressure is transmitted to the bell which, under the atmospheric pressure, falls, increasing the size of the gas openings, allowing more gas to pass and restoring the pressure in the outlet main. If the consumption decreases and pressure increases the bell rises and reduces the the size of the gas openings, and in this manner the pressure once set remains constant. When it is desired to alter the pressure in the outlet main to allow for periods of higher or lower consumption in the district, water is either added to or run off from the annular chamber in the bell.

Modern gas distribution aims at providing a constant pressure at the consumer's meter of 4 in. w.g., irrespective of load conditions. This is obtained by increasing the number of feeding points into the ordinary or low-pressure mains. At each point gas is passed through a station governor either from gas-holders at the works, or located in an outlying suburb or direct from high-pressure arterial mains fed by pumps from the works. These arterial mains will be of 12–48 in. diameter for distances under 20 miles, and be fed at initial pressures of 2–5 lb. per sq. in. For longer distances and for scattered areas, mains from 2 to 12 in. diameter would be used, and with initial pressures of 20–60 lb. per sq. in.

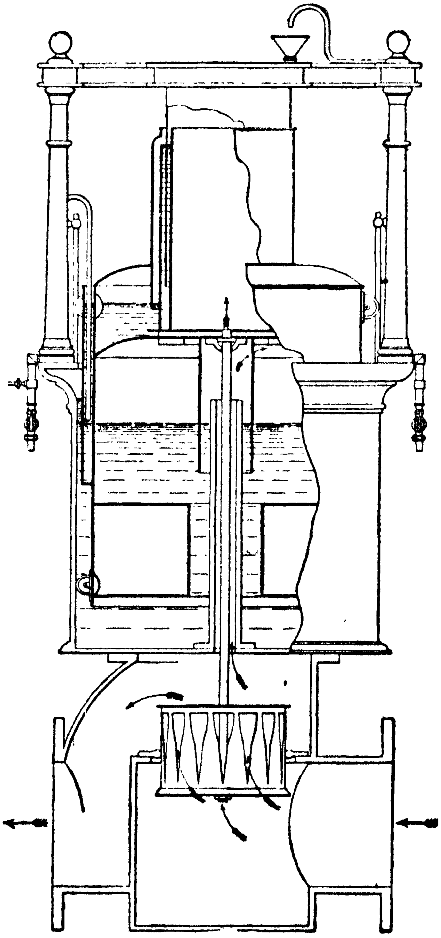


FIG. 26.—STATION GOVERNOR.

For pressures up to 15 lb. per sq. in. cast-iron gas mains are usually employed, but for higher pressures steel mains wrapped to prevent corrosion and with welded joints are commonly used.

RECORDING GAS CALORIMETRY.—The Gas Regulation Act, 1920, contained the provision that the apparatus prescribed for the official testing of gas supplied by undertakings having an annual output of more than 100 million cu. ft. should include a recording calorimeter. By the Gas Undertakings Act, 1934, it is decreed that from January 1, 1939, the prescribed apparatus shall, in the case of any thermal unit undertakers who have sold in the preceding year more than 5 million therms in the form of gas, and in the case of any other thermal unit undertakers, if it appears to the Board of Trade to be necessary, include a calorimeter for the production of a continuous record of the calorific value of the gas which is being supplied. Three instruments are prescribed for the larger undertakings. Each is of the flow type in which the heat developed by the combustion of a continuous supply of the gas to be tested is imparted to a continuous flow of heat-absorbing medium, the rise of temperature of which is continuously recorded upon a suitably calibrated chart. Means are included in the instrument for maintaining constant flows of gas and heat-absorbing medium, and the rise of temperature as recorded is proportional to the calorific value of the gas. The recorded calorific value is reduced to terms of a standard temperature and pressure by an appropriate design of the instrument.

In the Boys recording calorimeter (Fig. 27) the rate of gas burnt is maintained constant by means of a gas meter operated by a pendulum-controlled water-wheel, and is itself corrected for the varying temperature and pressure of the gas by the action of an expanding volume of air which operates a ball and plate gear-changing system. Water to the calorimeter is periodically weighed out by means of a tipping-bucket device, and its rise of temperature is, by a system of alcohol thermometers, transferred to a chart, the rulings on which are printed by the instrument itself. The heated water from the calorimeter passes through a cooler, over which air is blown by a fan attached to a hot-air engine, the latter also operating a pump which raises the water again to an overhead shallow tank.

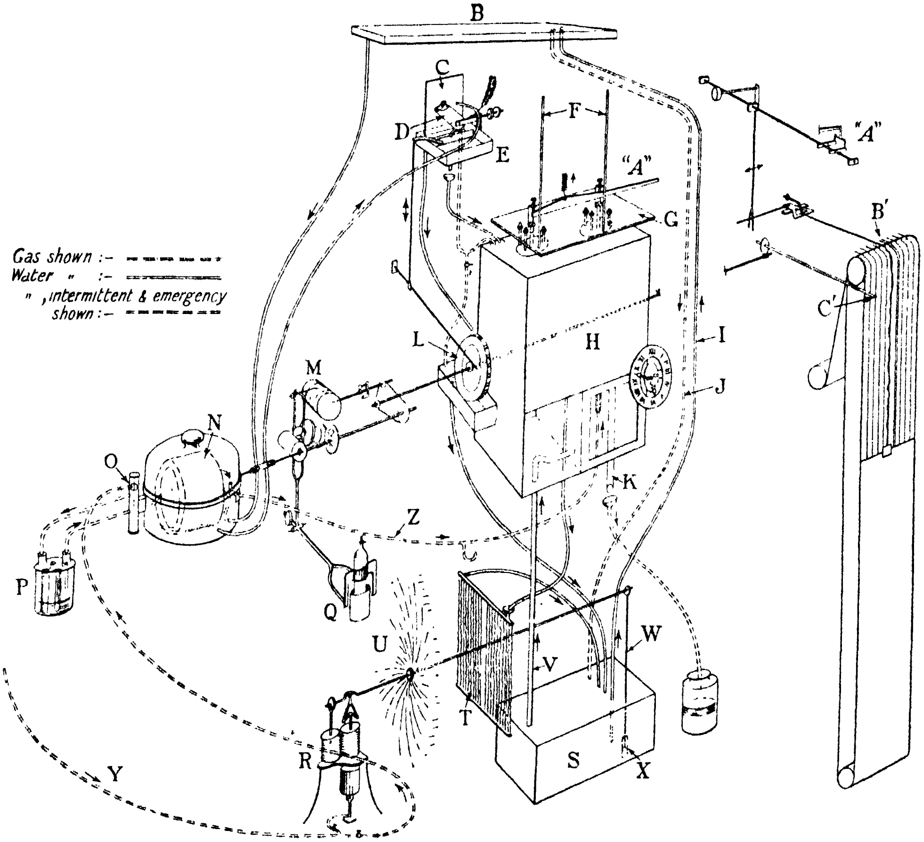


FIG. 27.—BOYS CALORIMETER.

In the Fairweather recording calorimeter gas is measured out by means of a meter connected to an escapement, and is burnt within a heat interchanger in construction very similar to that of the Boys non-recording calorimeter. To this a flow of water is supplied from an orifice acting under a head which, by the operation of an expanding volume of air, is made to vary in such a manner that the water flow is directly proportional to the factor necessary to reduce the gas volume to standard conditions of temperature and pressure. The rise of temperature of the water passing through the calorimeter is transferred to a suitably calibrated chart by means of a system of electrical resistance thermometers.

In the Thomas recording calorimeter an electric motor drives three meters contained in a tank, one supplying gas to the heat interchanger, another supplying air for combustion, while the third supplies a volume of air to which is imparted the heat developed in the heat interchanger. The rise of temperature of this heat-absorbing air is continuously recorded on a suitably calibrated chart by a system of differential recording resistance thermometers. In this instrument, correction for the varying temperature and pressure of the gas is not required, but slight changes in the specific heat of the heat absorbing air are corrected for by selecting for the resistance thermometers wire having appropriate characteristics.

In another type of recording calorimeter, of which the Sigma, Beasley and Calorgraph are typical, a measured volume of gas is burnt within a chimney from which free radiation is permitted, and into which a volume of air is drawn by natural draught. The rise of temperature of this air is made to operate a recording mechanism. These instruments record the net calorific value of the gas, but are usually set to read the gross value.

The Sigma and the Simmance Calorgraph, type R, instruments have been prescribed by the Gas Referees for the smaller undertakings, for use in conjunction with a non-recording calorimeter, in order to give the average calorific value for three months (*see* C. G. Hyde and F. E. Mills, "Gas Calorimetry," Ernest Benn, 1932).

Gas Quality.—All gas supplied for public use must by law be free from hydrogen sulphide. According to the Gas Works Clauses Act, the gas, when passed for 3 minutes over bibulous paper, previously moistened with lead acetate and dried in air free from hydrogen sulphide, shall not darken the paper. The rate of gas passage is fixed at 5 cu. ft. per hour (General Notification of Gas Referees). Since the formation of a brown stain of lead sulphide in this manner is an exceedingly delicate test for hydrogen sulphide, this means that for all practical purposes the gas passing the test is free from that impurity.

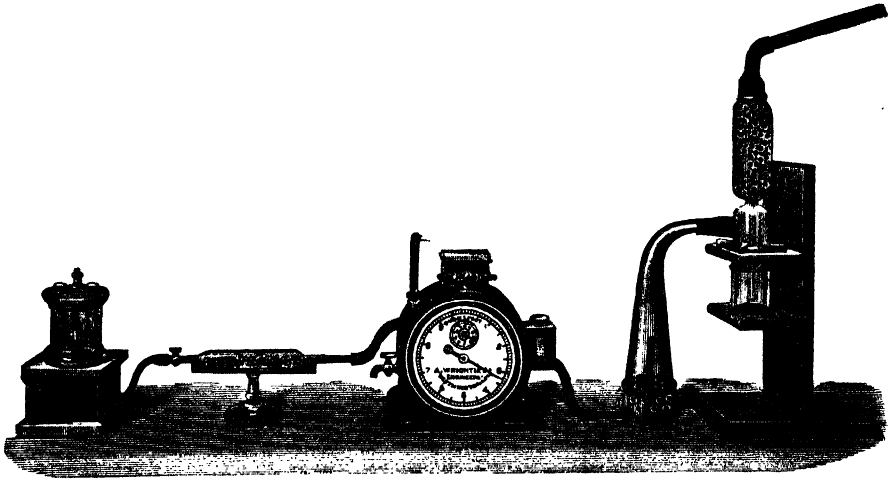


Fig. 28.—Total Sulphur Test.

A method for the estimation of the total sulphur present in purified gas is illustrated in Fig. 28. The gas is burned in a small Bunsen burner at the rate of 0·5–0·7 cu. ft. per hour until about 10 cu. ft. have passed, the flame being surrounded by lumps of commercial ammonium carbonate. The products of combustion together with ammonia pass by means of the trumpet tube into the glass cylinders provided with a tubulus at the bottom for connecting with the trumpet tube. The upper portion of the cylinder is filled with glass marbles, and from the top a wide bent glass tube is led which acts as a chimney and final condenser. A small tube from the cylinder drawn out to a jet conveys the condensed products to a flask or beaker placed in a shelf below. The sulphur dioxide resulting from the combustion of the sulphur compounds reacts in the presence of the moisture, the excess of oxygen and the ammonia to give a solution of ammonium sulphate. The sulphur determination is then carried out by washing out the apparatus with water and estimating as barium sulphate in the usual way, the amount being calculated as grains of sulphur per 100 cu. ft. In view of the risks of slightly low results, due to incomplete oxidation of the sulphurous acid primarily formed, a previous treatment of the solution with bromine is advisable. This method for the determination of total sulphur was formerly prescribed by the Metropolitan Gas Referees (Notification of the Gas Referees, 1918, 7). Other methods employed include aspiration of the products of combustion through sodium hypobromite solution followed by estimation as barium sulphate, or through neutral hydrogen peroxide, the sulphuric acid produced being determined by titration with standard alkali.

The major constituents of coal gas, namely, hydrogen, carbon monoxide, methane, ethane, unsaturated hydrocarbons (symbolised as CnHm), carbon dioxide, oxygen and nitrogen are normally estimated by measuring the change in volume or pressure following the removal of one constituent by some specific reagent. The carbon dioxide is removed with caustic potash solution; unsaturated hydrocarbons with bromine water, fuming sulphuric acid or an activated sulphuric acid; and oxygen with a solution of alkaline pyrogallol or chromous chloride. Hydrogen is usually removed by oxidation with copper oxide at 270°, while carbon monoxide can be either similarly oxidised or removed with solutions of acid or ammoniacal cuprous chloride. Methane and ethane are oxidised by passage over hot copper oxide or mixtures of copper oxide with other metallic oxides, or alternatively, are burnt with excess oxygen. Nitrogen is estimated by difference. The apparatus in general use for carrying out a complete gas analysis on the lines indicated above is that devised by Bone and Wheeler (Vol. II, p. 676) (*cf.* Hyde and Mills, *op. cit.*, p. 328).

The minor constituents of coal gas can be estimated either by a process of liquid fractionation (*cf.* W. J. Gooderham, J.S.C.I. 1937, **56**, 31T.) or by means of special tests. The various constituents in the percentage returned as " unsaturated " hydrocarbons include propylene and other higher olefins, diolefins, acetylene and aromatic hydrocarbons. Specific tests for individual constituents include colorimetric tests for the estimation of hydrogen sulphide, nitric oxide and metallic carbonyls, tests involving titrations with standard solutions for constituents such as ammonia, naphthalene, carbon disulphide, sulphur and hydrogen cyanide, and tests such as the cryoscopic estimation of benzole and precipitation of gum.

COMBUSTION CHARACTERISTICS.—Until recently the gas manufacturer has been concerned primarily with the production and distribution of gas of good quality. The increasing scientific design and production of appliances has now stressed the importance of a knowledge of the combustion characteristics. One important characteristic—calorific value—is already the subject of control, but performance is also affected by specific gravity and composition. The specific gravity of town's gas mixtures is in the main dependent upon the following factors:

(1) The percentage admixture with coal gas of carburetted water-gas, blue water-gas, producer gas or waste gas;
(2) The quantity of oil used for carburetting;
(3) The quantity of benzole extracted; and
(4) The inert content of the gas.

So far as calorific value and the specific gravity are concerned, the properties of any mixture of gases can be arithmetically calculated from a knowledge of the various constituents. This is not the case, however, with regard to the burning properties of a gas mixture, which are dependent upon the relationships between the flame velocity of the gas, the air-gas ratio and the velocity of the air-gas mixture. The appliance designer, having settled the ratio of primary and secondary air to secure proper combustion at normal and overload ratings having regard to the nature of the gas, is then faced with securing a defined shape and size of flame. In practice the height of the inner cone, which is a measure of flame propagation, is found to be the controlling factor. If this is or becomes too long, giving a soft flame, combustion may be impaired, unwanted flame contacts may occur and efficiency be lowered. Alternatively, too short a cone, giving a hard flame, will lead to noisy operation, risk of flashing back or blowing out and irregular control. Efforts have been made in this country and in Germany, the United States and Switzerland, to devise means of assessing these combustion characteristics. The first attempt at a practical solution appears to have been made by Hofsäss in 1919 (J. Gasbeleucht. 1919, **62**, 541), who employed a Bunsen burner with a fixed air inlet and deduced a " nominal flame velocity " from the height of the inner cone, which would serve to indicate the tendency of a gas to flash back or smother. In 1925, Ott, of Switzerland, introduced a burner in which the air port was calibrated so that the degree of opening required to produce popping back for any gas could be recorded on an arbitrary scale (*cf.* Schweiz. Ver. Gas-Wasserfach. Monats-Bull. 1931, 137). This " Ott Number " is used as is the " nominal flame velocity " of Hofsäss—to assess the combined effect of all the factors making for a hard or soft flame. More recently Czakó and Schaak (Gas-u. Wasserfach, 1934, **77**, 587) designed the " Prüfbrenner," in which the methods of Hofsäss and Ott are combined. A calibrated air port is adjusted to give a fixed height of inner cone and elaborate arrangements for reproducing the adjustments are made. In this country a simplified burner, based on the same principles as the " Prüfbrenner," called the " Aeration Test Burner," has recently been produced.

From the foregoing it will be evident that it should be a matter of concern to every gas undertaking that the gas manufactured will at all times meet those reasonable requirements which may be generally demanded as the result of progress in gas utilisation technique. At the same time the desirability of avoiding developments in appliances along lines which impose undue limitation of gas properties must receive consideration.

A practical example of the application of tests on combustion characteristics is seen in the work of P. C. Gardiner, who has conducted investigations with gases of varying Ott numbers in standard street lamps (*cf.* C. A. Deas, Gas. J. 1936, **216**, 672). When adjusted for a gas of high Ott value a considerably greater variation can be tolerated without lighting back than when the lamp is set for a gas of low value, thus indicating the desirability of keeping the Ott number as high as possible. It was found that mixtures of coal gas and producer gas have a higher Ott value than mixtures of coal gas and water-gas of the same calorific value.

The Joint Research Committee of the Institution of Gas Engineers and Leeds University has given a synopsis of available information upon gas quality, combustion characteristics and burner performance, designed to show which points may be regarded as definitely established, which require supplementary investigation and to what extent gaps in the existing state of knowledge require to be filled (Inst. Gas Eng. 1937, Comm. No. 166). Attention is also drawn to the work of C. A. Masterman and E. W. B. Dunning (*ibid.* Trans. 1931–32, 142) of H. Brückner and H. Löhr (Gas-u. Wasserfach, 1936, **79,** 17) and of the U.S. Bureau of Standards (1932, Rept. No. 446) to mention a few of the investigations on this subject. Valuable work on gaseous combustion has also been carried out by W. A. Bone and his co-workers and by Payman and Wheeler, to whose numerous works reference should be made in any study of this subject.

EMPLOYMENT OF COAL GAS.—At the present time coal gas is employed for a very great and increasing diversity of purposes. During the first 60–70 years of the existence of the industry it was almost entirely employed for illumination by burning it in open flame burners of various kinds. For illumination purposes now the light is obtained through the medium of the much more efficient incandescent burner, in which the burning gas raises to incandescence a mantle composed essentially of thoria, to which about 1% of ceria has been added (*v.* GAS MANTLES).

High-pressure installations are largely adopted for the outside lighting of public streets, etc.

A large proportion of the gas sold is now used for heating purposes, for example, heating with gas fires and cooking by gas. At the same time the use of gas has widened, and in addition to its uses in the private dwelling-house it is now established as a valuable medium for various heating, refrigerating and power purposes in restaurants, shops, factories, offices, etc. The adoption by many gas undertakings of a tariff system whereby purchases of relatively large quantities of gas could be made advantageously has aided expansion in these directions.

The many advantages of town's gas as an industrial fuel are now recognised. Steadily increasing quantities are employed for diverse purposes, including gas furnaces for metal melting, gas-fired kilns, annealing, etc. In general engineering practice the use of gas for carburising and general heat treatment work has been largely adopted. The value of purified town's gas or coke oven gas for furnace operation in the steel industry is discussed by J. W. Cobb (Chem. and Ind. 1936, 360).

H. H. and E. G. S.

GAS, LIQUEFIED HYDROCARBON (BOTTLE GAS).—In the United States, naturally-occurring hydrocarbon gases have long been employed as a fuel and illuminant, being distributed from the centre of production in the same way as coal gas. The commercial production of liquefied petroleum gas, comprising mainly propane and butane, is a later development and one which dates principally from about 1910. Such liquefied gas, once merely a by-product in the manufacture of natural gasoline, has now become an important primary product. The gas· available from natural sources is supplemented by that derived from petroleum-cracking.

In countries such as Great Britain, France and Germany, where natural sources of liquefiable hydrocarbon gas are lacking, the gas is obtained as a by-product of petroleum-cracking and of the hydrogenation-cracking of coal.

The process of winning liquefied hydrocarbon gas from natural gas comprises, in the first stage, a process of "stripping." Many methods have been devised to accomplish this (*e.g.* adsorption by activated carbon, refrigeration), but that which is now almost exclusively used is one of scrubbing the gas under pressure with gas oil (Vaiden and Fisher, Petroleum Engr. 1939, **10**, No. 10, 128). The resultant extract is separated from unabsorbed gases and fractionally distilled to give a residue of gas oil which is recycled, the requisite fraction of gasoline ("natural gasoline"), and a cut containing butane and the more volatile hydrocarbons. This latter fraction contains sulphur compounds; of these, hydrogen sulphide and some of the mercaptans are removed by an initial washing with caustic soda solution, while remaining mercaptans are rendered innocuous by washing with a solution of sodium hypochlorite.

After the hypochlorite treatment the cut is next washed with water, freed from mechanically-entrained water and rectified to give two fractions, one comprising the butanes and the other propane together with more volatile hydrocarbons. This latter cut is refractionated in a second column to give substantially pure propane, the distillate being taken off at a temperature sufficiently low to ensure its being anhydrous. Such dehydration is essential to avoid the risk of choking the consumers apparatus by ice or solid hydrates of hydrocarbons.

Liquefied gas arises as a by-product of the hydrogenation-cracking of coal and of the refining of petroleum; in the latter process it is obtained both directly from the crude petroleum and as the result of various cracking operations. The chemistry and technology of these processes are complex and will not be dealt with here; in general, the winning of the C_3 and C_4 hydrocarbons from the gases comprises (as for the natural gas concentrate) one or more stages of rectification and chemical purification. Gases from the cracking of petroleum contain not only saturated hydrocarbons but also a considerable proportion of olefins. The presence of these latter in liquid fuel-gas is of no great moment, since their calorific values do not differ greatly from those of the corresponding paraffins.

Properties and Use of Liquefied Hydrocarbon Gas.—The product as marketed in the United States usually contains 95% of C_3 hydrocarbons, C_4 hydrocarbons being added only as enrichers, and in quantities insufficient to raise the dew-point of the mixture to a temperature within the limits likely to be encountered. Small, adventitious amounts of such hydrocarbons as ethane and pentane may be present. Of the non-hydrocarbon constituents of the gas, water is present only in traces, while the content of combined sulphur is kept low to avoid corrosion of equipment, being usually of the order of 2–10 grains per thousand cu. ft. Traces of a strongly smelling substance such as ethyl mercaptan are added, to indicate leakages of this otherwise odourless gas.

Information concerning the precise composition of the gas marketed in Great Britain is lacking, but judging by its calorific value it would appear to contain a higher proportion of C_4 hydrocarbons.

Use as a Heating Fuel.—The approximate calorific value of liquefied hydrocarbon gas, of its constituents and of some other fuel gases are given below.

Gas.	Calorific value.[1] (B.Th.U. per cu. ft.)	Gas.	Calorific value. (B.Th.U. per cu. ft.)
Propane . .	2,500	Acetylene .	1,500
Propylene .	2,300	"*Calorgas*"[2]	3,250
n-Butane and *iso*butane .	3,300	Coal gas .	550
Butenes . .	3,000	Oil gas . .	1,300
		Air gas[3] .	110–220

[1] *Cf.* M. S. Kharasch, J. Res. Nat. Bur. Stand. 1929, **2**, 359; F. D. Rossini, *ibid.* 1934, **13**, 23; 1935, **15**, 357.

[2] The name under which liquefied hydrocarbon gas is marketed in Great Britain.

[3] Gas containing 12–19% by volume of gasoline vapour (Tulpov, J. Gen. Chem. Russ. 1939, **2**, 395).

The gas has a high and constant calorific value, gives high-temperature flames and combines many of the advantages of gaseous and liquid fuels. No generalisation can be made concerning whether it is preferable to such other sources of heat as coal gas and electricity. It can, however, be said that in all countries into which the gas has been introduced, the market for it is a rapidly expanding one, and that it is displacing oil gas and air gas.

In the United States it has found widespread industrial application, *e.g.* for welding purposes and for firing metallurgical furnaces. Gas (*e.g.* coal gas) manufacturers and users employ liquefied petroleum gas to meet difficulties arising from abnormal conditions, such as failure of supply and unexpectedly high consumption. Domestic consumption of the gas (for heating and lighting purposes) is also large. Small towns and villages are frequently supplied from a central tank holding perhaps 15,000 gallons of liquid, which is periodically refilled from tank-cars. Means are provided for vaporising and metering the gas, and for supplying it to consumers either neat or, as is less frequently the case, diluted with air to a calorific value of 500–900 B.Th.U. per cu. ft. (W. T. Ziegenhain, Oil and Gas J. 1938, **37**, No. 7, pp. 20–21). Where consumers are sparsely scattered, it is usual to supply each one individually with one or two tanks, containing 2–3 months supply. These are refilled either from a central filling station or from a mobile service tank.

Although detailed information concerning the market for liquefied gas in Great Britain is not available, it would seem that both industrial and domestic use is widespread, and that the total consumption is large and is rapidly increasing.

Use as a Fuel for Internal Combustion Engines.—Both the calorific value and anti-knock properties (Lovell, Campbell and Boyd, Ind. Eng. Chem. 1934, **26**, 1105) of the C_1 to C_4 aliphatic saturated and of mono-olefinic hydrocarbons are high. Consequently they are at least potentially valuable fuels for internal combustion engines. The storage difficulties which would be associated with the use of gases with such low critical temperatures as methane and ethane have apparently not yet been surmounted, but the C_3 and C_4 hydrocarbons have found considerable application as automobile fuels, particularly in the United States, Germany and Italy. In California, 15,000,000 gallons of this fuel were consumed in automobiles during 1937 (Wickstrom, Gas, 1937, **14** (7), 55–57) while in Germany, where the quantity of coal treated by hydrogenation is increasing, a large proportion of the by-product C_3 and C_4 hydrocarbons is being similarly utilised (Norman, Oil and Gas J. 1940, **38**, No. 36, 14).

The wider aspects of the utilisation of liquid hydrocarbon gas can only be touched upon. Propane has found considerable application as a solvent for the dewaxing of lubricating oils. The butanes have been used as a working fluid for refrigerators, while *iso*butane is an important raw material for the production of high-octane fuels by catalytic alkylation (*i.e.* the reaction of olefins with *iso*paraffins in the presence of sulphuric acid). Propane and the butanes can be catalytically dehydrogenated to propylene and the butenes, which in their turn serve as starting materials for the manufacture of propyl alcohol, polymer gasoline, etc.

Bibliography.—The literature concerning liquefied hydrocarbon gas is large, and for the most part deals with practice in the United States. This particular aspect has been well summarised in a monograph by E. L. Weaver (U.S. National Bureau of Standards, 1938, Circular No. 420), while detailed statistical information is available in the Mineral Market Reports issued by the U.S. Department of the Interior, Bureau of Mines. Progress made in the general field of liquefied gas manufacture and consumption is summarised in "Annual Reviews of Petroleum Technology" (published by the Institute of Petroleum).

F. H.

GAS DEFENCE *v.* CHEMICAL WARFARE DEFENCE.

GAS MANTLES.—Modern gas lighting has been made possible by two important discoveries: the atmospheric burner developed by Bunsen and the luminosity acquired by certain metallic oxides when heated in a flame. Berzelius, who discovered cerium in 1803 and thorium in 1825, observed the incandescence of the oxide of thorium when heated. Thus it is to him that we owe the discovery of the compounds, sometimes called the rare earths, which form the basis of the present day gas mantle. The development of incandescent gas lighting extended over many years of the last century and a brief account of the more important advances is given in the following paragraphs.

In 1826 Gurney found that a brilliant light was obtained by the impact of the oxy-hydrogen flame on a piece of solid lime, and Drummond employed this newly discovered lime-light in a practical form in 1827. Talbot, in 1835, noticed that when a piece of blotting paper was saturated with a solution of lime salts and then incinerated, it left a skeleton of ash which glowed brightly in the flame of a spirit lamp. This and the earlier experiments showed that if a refractory material, such as lime, could be obtained in coherent filaments, a moderately hot flame would raise it to brilliant incandescence.

An interesting forerunner of the present day mantle was proposed by Cruickshank in 1839. He constructed a device of platinum wire suitably shaped to the flame. The wire was coated with a covering of refractory oxides such as lime or thoria and the cage was heated by means of a water-gas flame. In 1848 Gillard employed small mantles made from fine platinum wire raised to incandescence by the flame of burning hydrogen, and some years later a somewhat similar attempt was made by Edison. He patented, in 1878, the coating of platinum wire with the oxides of zirconium and cerium. All these systems failed owing to the high price and rapid deterioration of the platinum.

A mantle of magnesia was developed by Clamond in 1882. This was made by grinding powdered magnesia into a paste with water containing magnesium acetate. When moulded into the form of a basket and ignited, the heat decomposed the acetate leaving cemented particles of magnesium oxide. These mantles gave a good light but were too fragile for common use. Finely powdered magnesia was used also by Fahnehjeln of Stockholm in 1883. His method was to mix the magnesia with a plastic material and form solid rods by extruding the paste through a die; the prepared rods of refractory material in the form of a comb were suspended over a water-gas burner. Fahnehjeln's combs, as they were called, gave a light equivalent to about four candles per cubic foot of gas consumed and they were used fairly extensively for domestic lighting.

The introduction by Bunsen of the atmospheric burner, about 1855, greatly assisted the application of town's gas for heating purposes and some thirty years later Auer von Welsbach made the discoveries which gave the world the modern incandescent gas mantle.

The early eighties marked the commencement of Welsbach's series of discoveries. At this time he was engaged in an examination of the rare-earth substances, and in the course of his researches in 1884 he found it necessary to make a great number of observations with the spectroscope. Part of his method was to heat, in a Bunsen flame, a platinum wire that had been previously dipped in a solution of the salts to be examined. Welsbach found that the light obtained in this way was not sufficiently permanent or intense for his purpose, and he discovered that a cotton thread when dipped in a solution of rare-earth salts, dried and subsequently incinerated, left an oxide skeleton which glowed brightly when heated. Moreover, although the cotton fibre burned away, the rare-earth oxides were left behind in a coherent thread and did not fall to powder.

Welsbach perceived the importance of his discovery and, after a further series of experiments, he found that a cotton fabric when shaped into a sleeve and impregnated with a solution of the nitrates of the rare earths, dried and finally burned over a Bunsen flame, left a comparatively strong framework of oxide that emitted a light of considerable intensity. Welsbach's first patent, taken out in 1885, mentioned the use of the oxides of lanthanum, yttrium, zirconium and magnesium, and a year later a German patent protected the use of thorium salts.

In the early mantles no great care was taken to purify the materials used because the separation of the rare earths was difficult, consequently the light emitted varied in colour showing green to orange tints according to the variations in the composition of the oxide mixtures in the mantle. The amount of light given by these mantles rarely exceeded six candles per cubic foot of gas consumed, and they were so fragile in character that they were unable to withstand slight shocks. Thus the first Welsbach mantles were not a commercial success and showed no great advantage over the electric carbon filament lamps which were rapidly developing at this time.

About 1891 Welsbach was examining the light given by the oxide thoria when he found that the intensity of illumination became less and less as the thorium salts were made purer. By this discovery he was led to make a further important contribution to the science of gas lighting by observing that a filament of pure thoria had a relatively low illuminating value, but a very much greater degree of light emission was rendered possible by the addition of small quantities of other rare-earth oxides. Pursuing his investigations Welsbach added gradually increasing quantities of ceria to pure thoria and determined that mere traces of ceria endowed the ash with the wonderful light-giving property possessed by the modern mantle. Welsbach announced this result in a patent in 1893 and since that time the "Welsbach mixture" containing 99% of thoria and 1% ceria has been universally used in mantle manufacture. Although many thousands of experiments have since been made, this mixture has remained beyond doubt the most efficient (Fig. 1).

After the introduction of the Welsbach mixture progress became rapid although the mantles themselves left much to be desired. Their chief defect was that during use they were found to decrease rapidly in strength and light-giving power, besides shrinking in length and diameter. The oxides which can be used in mantle making are limited in number owing to the fact that they must be able to withstand the temperature of the flame for long periods, and the selected oxides must not be liable to excessive shrinkage during the burning away of the original fabric. The oxides of aluminium, beryllium, thorium and zirconium are possible substances for the basis of a mantle, but of these, aluminia and zirconia are liable to considerable shrinkage and volatilisation, so that the life of the mantle is shortened by the gradual wasting away of the threads of the skeleton. The oxide of thorium is refractory under the heat of a Bunsen burner for a much longer time than any other known oxide and in the conversion, by ignition, of thorium nitrate into thoria, the material expands to 10 times its original volume. For these reasons thoria constitutes the basis of all present-day incandescent mantles.

When Welsbach made the first mantles from thorium salts, the rare earths were obtainable only in small quantities and from such minerals as thorite and orangite, found in Scandinavia, but with the increasing demand a search was made for more abundant and cheaper sources of the element. It was soon found that monazite, consisting largely of phosphates of the cerium group of metals, was very widely distributed over the earth's surface, and the discovery of the monazite sands of Brazil and the Carolinas soon gave the industry ample supplies. In the early years of this present century immense deposits of monazite were found at Travancore in Southern India; these sands contain about 50% of the mineral, and the monazite is rich in thorium oxide. For use in mantle manufacture the thorium salts must be of a very high degree of purity, and the separation of the thorium and cerium from monazite is a process of considerable technical difficulty.

Investigations into the rapid depreciation of the early mantles led to the important discovery that the structure of the cotton contributed to the rapid shrinkage of the mantles when in use. Cotton yarn is spun from a large number of comparatively short fibres, twisted together during the spinning process to form a continuous thread. The skeleton of oxide left after incineration of the cotton retains the physical structure of the original fabric, thus the coherent ash of a cotton mantle is composed of a large number of short twisted lengths (Fig. 2). It is largely the effort of these short threads to untwist themselves which caused such mantles to lose their shape. When greater care was taken to obtain cotton with a long fibre, mantles made from this superior material showed a distinct improvement in durability and also in light-emissivity.

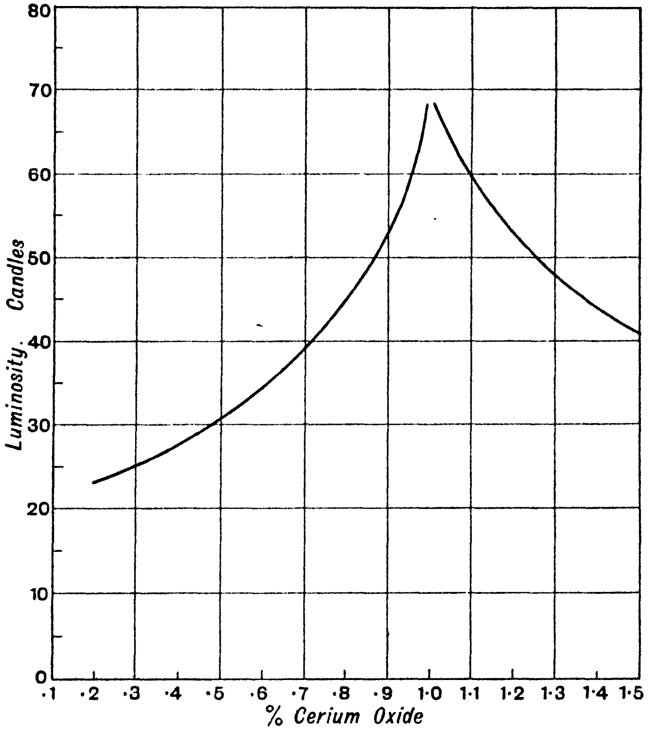


FIG. 1.

The introduction of ramie fibre in place of cotton by Buhlmann in 1898 marked an important advance in the efficiency of gas mantles. Ramie, or China grass (*q.v.*) as it is sometimes termed, has now almost entirely replaced cotton for mantle manufacture. The ramie fibre is obtained from the tschuma plant which in its raw state resembles the common nettle of Europe, and is exported chiefly from China. When the stems of this plant are freed from their glutinous coating they leave long straight fibres of superior strength and durability. These fibres require less twisting than cotton, and mantles made from ramie do not deteriorate when heated.

In 1901 Plaissetty developed the use of artificial silk. As the fibres of this material are practically continuous there is very little twist required in the spinning and this substance makes an excellent fabric for the manufacture of gas mantles (Fig. 3). The filaments of modern artificial silk made by the viscose process have a solid structure and are unlike the tubular fibres of cotton or ramie. This difference in the structure of the thread has an important bearing on the ultimate strength of the mantle, although the thread is only used as a temporary support for the rare-earth salts.

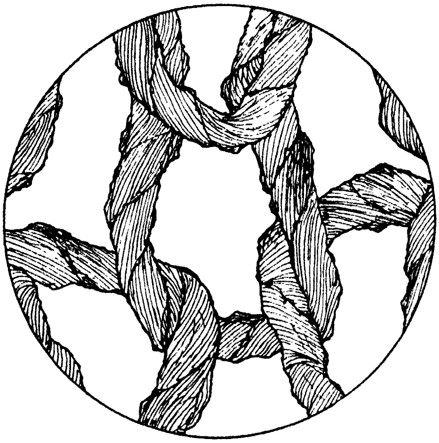


FIG. 2.—ASH OF COTTON MANTLE.

As the materials employed in the making of artificial silk are relatively pure the amount of mineral ash left after incineration is negligible, and silk fabrics do not require the thorough washing process that is essential when vegetable fibres are used. Because of its solid structure artificial silk behaves differently from vegetable fibres. It absorbs the impregnating solution comparatively slowly, and several hours soaking at normal temperatures are required to impregnate the fabric completely. Further, a much finer yarn is employed for silk mantles than for those made from ramie and therefore the ratio of the weight of yarn to absorbed nitrates is much less. Hence if the viscose fabric containing nitrates is burned in the usual way the incineration is very rapid with the result that the oxide skeleton falls to powder. In Plaissetty's process the impregnated artificial silk is dried slowly and then treated with ammonia solution. This method of "fixing" the oxides by ammonia gives good results and the resultant mantles are strong and flexible. The action of the ammonia is to convert the nitrates into insoluble hydroxides and the ammonium nitrate produced in the reaction must be removed by thorough washing in distilled water.

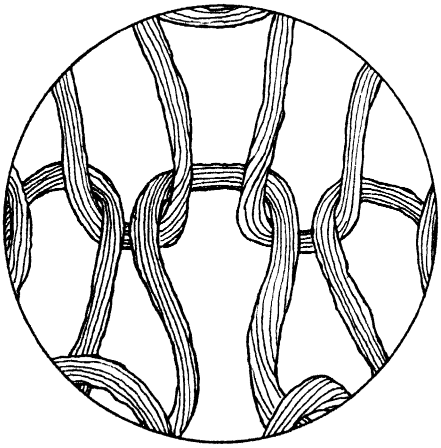


FIG. 3.—ASH OF ARTIFICIAL SILK MANTLE.

In the commercial manufacture of mantles the greatest possible care must be exercised at every stage. The fibre used to form the thread must be of even quality and thickness. The selected thread is knitted into a long tube of fabric, known as a "stocking," by machines provided with a number of needles disposed in a circle and fed by one or more spools of yarn. After leaving the knitting machines the cotton or ramie stockings contain impurities to the extent of 1%, and special care is needed to eliminate them as their presence even in small quantities adversely affects the strength and lighting power of the mantle to a remarkable degree. The washing of the stocking made from vegetable fibre must be exceptionally thorough if a good quality mantle be required. The fabric is well washed with boiling alkali solutions, rinsed in water and dilute nitric acid for several hours, and finally washed in distilled water and partly dried in a centrifugal machine. The drying is completed by hanging the fabric in chambers through which warm dust-free air is circulated. The washing process occupies 2 or 3 days and the mineral matter in the fabric is reduced to less than one part in ten thousand.

The washed and dried fabric is now ready to act as a temporary support of the rare-earth compounds which alone will constitute the skeleton of the finished mantle. The impregnation of the stocking with the "Lighting Fluid" is carried out by immersing the fabric in a solution consisting mainly of thorium and cerium nitrates. The exact composition of the lighting fluid varies slightly according to the nature of the mantle required, but owing to the marked effect on the light-giving power of even small deviations from the standard mixture it is of the greatest importance that the proportion of thorium oxide to cerium oxide should be in the ratio of 99 to 1. The thorium nitrate is dissolved in distilled water to form a 30% solution and the calculated amount of a standard cerium nitrate solution added. With ramie and cotton fabrics it is usual to add a small proportion of beryllium nitrate in such quantity that the final ash contains about 0·5% of beryllium oxide. The addition in small amounts of the nitrates of other metals such as aluminium, magnesium and calcium is sometimes made, the function of their oxides being to strengthen the ash by causing a partial fusion of the ash skeleton. A suitable formula for the lighting fluid for the impregnation of ramie and artificial silk fabrics is as follows:

	g.
Thorium nitrate . . .	1,000 (48·0% ThO_2)
Cerium nitrate . . .	12
Beryllium nitrate . . .	4
Aluminium nitrate . .	1
Distilled water . . .	2,000

The weight of oxide, which forms the inverted mantle in general use, is about 0·5 g. A ramie fabric takes up about its own weight of solution before becoming saturated, whereas artificial silk will absorb more than twice its weight of the fluid before impregnation is completed. The time required for soaking the fabrics in the solution is 5 minutes in the case of cotton and ramie and 12 hours for artificial silk. After immersion the lengths of stocking are passed through carefully adjusted hard rubber rollers which squeeze out the surplus solution and allow the fabric to retain the exact quantity of lighting fluid calculated to give the correct weight of ash in the final mantle. The amount of rare-earth oxides required for the various types of mantles must be very rigidly controlled, for if more than the correct quantities are used the light-giving power of the mantle is seriously reduced without any corresponding gain in strength; alternatively if the oxide skeleton is less than the correct weight, the light-emissivity is high, but the mantle is too fragile for practical use. After impregnation the lengths of stocking are dried by festooning over glass rollers in a room through which a current of warm dust-free air passes.

In the case of cotton and ramie fabric the lengths of dried impregnated stocking are now ready for cutting into pieces of between 1–3 in. in length according to the type of mantle required. Artificial silk has, however, to undergo a fixing process in which the dried, impregnated lengths are immersed in a solution of ammonia. This solution is kept well stirred to allow the free diffusion of the ammonia through the fabric. The conversion of the nitrates into the insoluble hydroxides is rapid if the ammonia solution is kept agitated, thus after a few minutes immersion the "fixed" stocking is ready for a thorough washing in distilled water to remove all traces of the ammonium nitrate formed in the reaction. The treatment of artificial silk now differs very little from that of cotton or ramie fabrics and the dried lengths are cut into short pieces.

The strips of stocking are now stamped with a trade mark, if this is desired on the finished mantle. The solution usually employed for this purpose leaves, after burning-off, an indelible and highly refractory residue of the brown didymium oxide, a suitable formula for this solution is:

	g.
Didymium nitrate	1,000
Glycerin	250
Industrial alcohol	500
Methylene blue	3
Distilled water	500

The normal inverted mantle is supported from the burner by a clay ring made from a specially prepared refractory material containing a high proportion of magnesia. Before tying one end of the short length of mantle fabric to the ring with an asbestos thread, the end is strengthened, to a depth of half an inch, by a hardening fluid. A suitable mixture for this purpose being:

	g.
Thorium nitrate	1,000
Aluminium nitrate	700
Magnesium nitrate	700
Sodium pyroborate	12
Acid magenta	3
Distilled water	2,500

The hardening solution is applied to the head of the mantle by means of mechanically operated rubber rollers which are wetted with the mixture supplied from a small tank. The treated end of the fabric is now secured to a groove in the clay ring by means of a double band of carefully selected asbestos twine, the asbestos binding being just loose enough to allow for the contraction that occurs in the subsequent heating. The remaining or lower end of the strip of stocking is now sewn with impregnated threads of the fabric and drawn together in small pleats to close the bottom of the mantle. In the upright type of mantle which is supported from a central rod or fork of compressed magnesia, a strip of impregnated cotton gauze is sewn over the edge at one end of a 6 in. length of the stocking, and the hardening fluid is applied to this end, which will form the top of the mantle and which is most liable to breakage. The top is then finished by pleating with an asbestos thread drawn through the meshes of the fabric and a loop of thread is left to engage with the head of the supporting fork. During recent years machines have been largely employed for all these operations, but in the best quality mantles they are still carried out by skilled needlewomen as very small differences in the fabric have considerable effect on the completed mantle. Trained operators can make allowances for any variations due to slight differences that may occur in the knitting, washing and impregnating processes.

The next operation is the "burning-off" or incineration of the knitted fabric and the transformation of the thorium and other salts into the refractory oxides which form the final ash skeleton. The pliable mantle is shaped on a wooden former and then supported by a metal hook or jig. The wooden mould is removed and a gas flame is applied to the top of the mantle which ignites readily and burns steadily downwards under the control of an operator who adjusts the air entering a ventilated hood. The "burning-off" process requires great care because, as incineration proceeds, the mantle shrinks and too rapid burning will cause uneven contraction and the development of cracks in the fragile ash network that remains. The organic substance of the fabric is completely consumed in 4 or 5 minutes and the oxides which remain retain the form of the original knitted fabric.

The mantle is now in an extremely fragile condition and the next process of shaping and seasoning requires great care and experience to ensure that the delicate ash framework is not damaged or mis-shapen. The machine for shaping the mantles consists of a row of gas burners mounted on a metal frame, which is equipped with a mechanical device for raising and lowering the burners. Each burner is fed with a mixture of gas and air under pressure. The flame is started with a comparatively low-pressure of air and this is gradually increased so that the flame exerts a steady pressure on the mantle, which is held in position by a support of heat-resisting metal. As this operation proceeds the pressure of the flame slowly moulds the oxide skeleton into a uniform shape while the toughness and elasticity increase as the heating continues. The seasoning or hardening of the ash lasts from 3 to 5 minutes according to the size of the mantle being treated.

The manufacture of the mantle is now complete but, to protect the fabric from the hazards of transport, the mantle is dipped into a solution of collodion which coats the ash with a thin film of varnish. This covering is a specially prepared solution of cellulose nitrates dissolved in a mixture of alcohol and ether to which camphor and castor oil have been added to prevent shrinkage during drying. The highly inflammable solvents are removed by drying the mantles in a well ventilated hood, in which the air is heated to a temperature of 50°C. The composition of a suitable collodion varnish is as follows:

	g.
Alcohol (Industrial)	1,000
Ether	800
Camphor	72
Castor oil	40
Cellulose nitrates	35

After varnishing and drying, the mantle is resistant to shock and vibration. In this condition it is packed and transported and the collodion film is easily burnt away when the mantle is required for use. Some types of artificial silk mantles, especially those used with high-pressure lamps, do not undergo the processes of burning-off and shaping, but are sent out from the factory in the soft unburned condition. In this case varnishing is unnecessary and the mantles are incinerated and shaped by the gas pressure of the lighting burners, on which they are to be used.

Before leaving the works, experienced examiners gauge the size and scrutinise the fabric of every mantle. In order to pass these tests the mantles must be uniform in length and shape, for a tolerance of one-eighth of an inch only is permissible with a good quality product, and the ash must be entirely free from defects.

Within recent years the manufacture of gas mantles in England has been largely confined to a few well-equipped factories, each of which is provided with a testing room. In this department tests for durability and illuminating power are made on each batch of the finished product. The durability of the mantles is determined by observing their behaviour when in use for at least 1,000 hours and their resistance to vibration is ascertained by testing the mantles on a shock machine. The illuminating power of the mantles is determined by means of one of the well-known types of photometers used in conjunction with a burner, the gas consumption of which is carefully controlled.

The discovery and development of the incandescent gas mantle revolutionised the economic production of light from coal gas, and Welsbach's system was immediately challenged by several inventions which sought to evade the Welsbach patents. A great deal of ingenuity was expended in devising suitable alternatives, chief of these being a process invented by De Mare in 1894, his idea being the use of refractory plumes suspended over a Bunsen burner. Again in 1908, Rene Leigle carried this idea further and developed the "*Hella*" bushlight, Fig. 4, consisting of a tassel of refractory rods made from the oxides of thorium and cerium. The filaments were raised to a brilliant incandescence and it was claimed that the rods had a long life and an efficiency equal to that of the conventional mantle. The commercial success of the Welsbach mixture led also to the use of thorium

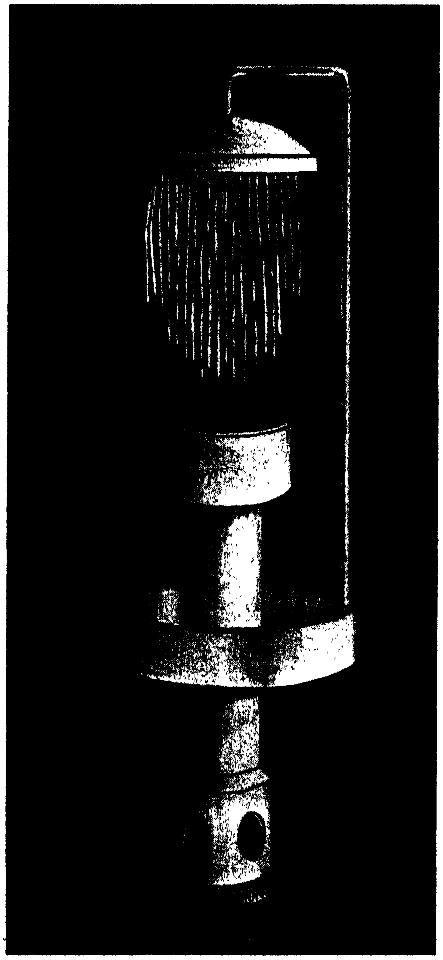


FIG. 4.—HELLA BUSHLIGHT.

and cerium salts under new names not specified by the Welsbach patents, and numerous mixtures of compounds containing almost every known element were tried in efforts to equal or improve the new method of illumination. All these attempts failed, and the Welsbach formula has remained.

Before 1900 all the mantles used were of the upright type, but owing to the slightly conical shape of the fabric the maximum light was given above the level of the burner and the shadow of the fitting was thrown on the surface immediately below the mantle. Special types of reflecting shades and glass chimneys were introduced to overcome this defect and the efficiency of the early upright burners was much improved by Bandsept and Danayrouze. In 1897 Kern introduced a notable burner that is still known by his name. In this burner the gas issues from an injector into a suction chamber consisting of two cone-shaped tubes joined at their smaller ends. This device was found to increase the proportion of air drawn in with the gas and this burner gave more light from the upright mantle than any other burner than in general use.

About 1900, Kent developed the use of the inverted burner and mantle. This type rapidly became popular because, in this case, the maximum light is directed downwards and there is no shadow from the fitting. Other advantages are that the inverted mantle, being suspended from lugs on the burner tube, is less likely to be injured by vibration than an upright mantle; and with the inverted mantle it became possible to apply, in a simple manner, the principle of recuperation to gas burners.

The light output from a gas mantle is a function of the temperature of the mantle, and the higher the temperature of the fabric the greater is its light-emissivity. By recuperation, that is, using the heat in the hot gases leaving the flame to preheat the mixture of gas and air passing through the burner, the flame-temperature and consequently the light-emission is increased.

A further improvement in the light emitted by the Welsbach mantle was made possible about 1908 by the introduction of inverted mantles in combination with high-pressure gas burners. These units work at from 50 to 120 in. water-gauge pressure, and the amount of light obtained is from 3 to 4 times as great as that obtained from the original low-pressure upright type of mantle.

The recent development of high-pressure gas supply and the preheating of the gas mixture have notably increased the illumination given by the mantle, but a natural upper limit is set to the brightness obtainable by the tendency of ceria to volatilise at very high temperatures.

In recent years it has become the custom to express the light output from gas mantles in lumen-hours per cubic foot of 500 B.Th.U. gas. The "lumen" is the luminous flux per unit solid angle, or $\frac{1}{4\pi}$ of the total flux, emitted by a point source of one candle. The lumen output of a mantle, therefore, is the average candle power multiplied by 4π. The following table represents the light emitted by mantles in present day practice.

Type.	Efficiency in lumen-hours per cu. ft.
(1) Low-pressure, upright . . .	100
(2) Low-pressure, inverted . . .	150
(3) Low-pressure, inverted, preheated	200
(4) High-pressure, inverted, preheated	370

The composition of gases supplied to burners may differ, but providing the rate of heat supply is the same the amount of light given by the mantles is approximately equal.

In the last decade much ingenuity has been expended in adapting the mantle to modern needs. Mantles are now available, the light from which approximates to daylight, and these are useful where colour matching has to be carried out in artificial light. A reduction to 0·1–0·25% in the proportion of cerium oxide present in the mantle gives a light having a spectral composition nearer to daylight than the light given by ordinary mantles made from the Welsbach formula, though they do this by some sacrifice in total light-output.

Modern street-lighting practice requires an even distribution of light over the surface of the roadway, and in attempts to achieve this, reflectors and refractors are often incorporated in the lamps. In 1935 attention was directed to the possibility of altering the shape of the light source. Hitherto gas mantles had been invariably cylindrical in shape, the shape having arisen from the desire to fit the flame which issues from a nozzle with a round orifice. There is, however, no fundamental reason why all burner nozzles should have round holes or why in consequence all mantles should be cylindrical. It is only the surface of the flame which comes in contact with the mantle and the cylindrical flame happens to be the one which possesses the minimum surface. When the shape of the cylindrical mantle is altered the surface is increased and the amount of mantle fabric heated by the flame is greater. By making the burner nozzle in the shape of a slot instead of in the form of a round hole, and the mantle as a bag with two flat rectangular sides of greater length than depth, it is possible to obtain, in the desired direction, an illumination 2½ times as great as that obtained with the cylindrical type of fabric using the same amount of gas. Three modern types of mantles are shown in Fig. 5.

Another modification of the Welsbach mantle available to-day is the "*Spiderless*" or moulded mantle. In this type the inverted mantle is not fashioned from a tube, but is pressed with the aid of moulds from a rectangular piece of impregnated fabric. This piece of material, now in the shape of a hemisphere, is tied to a ring, trimmed and then shaped in the conventional manner.

Toward the end of the last century the possibility of making "self-lighting" mantles began to be considered. Platinum precipitated in the metallic state from a solution forms a powder, called "platinum black," which possesses sufficient catalytic activity to cause oxygen and hydrogen to react at atmospheric temperature. The heat of reaction is sufficient to cause ignition of a gas jet impinging upon the catalyst. A self-lighting mantle is formed by attaching to the mantle ash a small pellet composed of a mixture of platinum black and argillaceous earth. The device does not usually have a long life as the platinum black loses its activity after prolonged heating.

Several theories have been advanced to explain the remarkable light-giving properties of the Welsbach mantle and the more important may be considered under the headings of I. selective radiation, II. low heat losses and III. catalysis.

I. When heated to the same temperature platinum emits a larger proportion of useful light rays than does iron oxide, and such substances as platinum which radiate light and heat, are often described as selective radiators. The selective radiation theory contends that the incandescent mantle is an example of this phenomenon and the thoria-ceria mixture employed is remarkable for the high proportion of energy which is radiated in the visible spectrum.

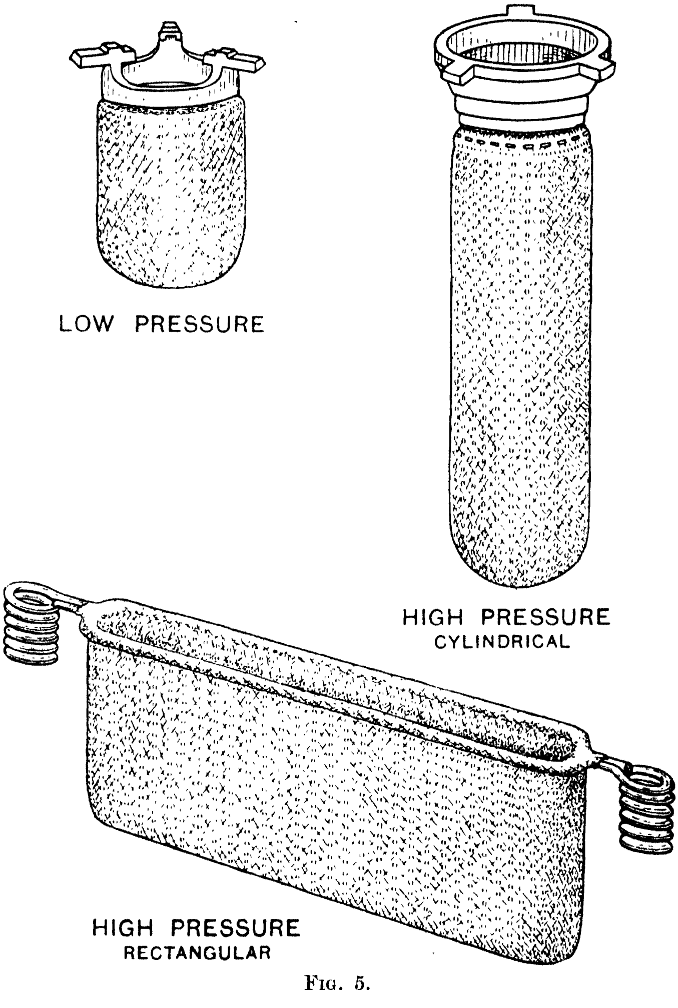


Fig. 5.

II. The mantle in the flame is in a state of thermal equilibrium, receiving heat by conduction and losing heat by radiation. Pure thorium oxide has a low capacity for radiating heat, and in consequence of this a mantle consisting mainly of this oxide reaches a higher temperature in the flame than would a mantle made from a good radiator such as iron oxide. Ceria, on the other hand, has great radiating power, and the addition of large proportions of ceria to the Welsbach mixture causes a rapid cooling of the mantle. The cerium content of the mantle must therefore be controlled with great accuracy. It is the low emissivity of thoria in the infra-red range and the high temperature of the radiating source which, according to this view, leads to the high luminous output.

III. The catalytic effect of the thoria-ceria mixture on the rate of combustion of the gases at the surface of the mantle has been investigated by several workers. Killing and Bunte pursued this line of explanation and suggested that the widely distributed ceria caused an accelerated reaction between the flame gases. Some workers are of opinion that it is because of this catalytic action that a high local temperature and increased luminosity is produced.

References.—Haber (J.S.C.I. 1914, **33**, 51); Ives, Kingsbury and Karrer (J. Franklin Inst. 1918, **186**, 401, 585); Swan (J.C.S. 1924, **125**, 780); Chandler (Gas World, 1937, **107**, 218).

A. J. P.

GAS, POISON *v.* Chemical Warfare.

GAS WARFARE *v.* Chemical Warfare.

GAS, WATER. Water gas is the term applied to the gaseous mixture of hydrogen and carbon monoxide formed by the passage of steam through incandescent carbon. Until recent times its manufacture on a large scale has been conducted almost entirely by gas undertakings for the purpose of admixture with coal gas as described above (*see* Gas, Coal, this Vol. p. 469). To-day considerable quantities of hydrogen are required for the production of synthetic ammonia, synthetic fuels, methanol, etc., and, since water gas affords a ready and economic source of this gas, large water-gas plant are now operating for this purpose. Those at the Billingham Works of Imperial Chemical Industries, where, in addition to the production of synthetic ammonia, large quantities of coal and of tar oils are hydrogenated, may be cited as examples.

The production of carburetted water gas as an adjunct to the manufacture of coal gas having been already described, the following description will be more particularly directed to the production and utilisation of uncarburetted or "blue" water gas. At the same time it will be realised that the two are in many aspects so closely related that it is not possible to discuss one without reference to the other. The matter below should therefore be read in conjunction with the article above mentioned.

The interaction of steam and incandescent carbon was probably discovered by Fontana in the eighteenth century and was certainly known to Lavoisier who, in 1793, recorded the production thereby of hydrogen and carbon monoxide.

The first known attempt to utilise water gas on a commercial scale was made by Ibbotson, who in 1824 sought to increase the volume of gas distilled from coal gas retorts by injecting steam into the red-hot coke remaining at the end of the period of carbonisation. This idea was revived on many occasions, but so long as the horizontal retort remained in general use for the purpose of distilling coal, the production of water gas in this way was found to be impracticable. With the introduction of the vertical retort, and to a less extent following the use of more closely packed horizontal retorts, this system of "steaming" received attention again and has now been widely adopted with success.

Early attempts to manufacture water gas by a continuous process, in which steam was passed through coke contained in an externally heated generator, failed for the reason that the coke must be maintained at a relatively high temperature in order to make water gas successfully. With temperatures of the order of 600°, the reaction between the steam and the carbon is mainly according to the reaction

$$C+2H_2O=CO_2+2H_2$$

and it is only when the temperature exceeds 1,000° that the reaction closely approaches

$$C+H_2O=CO+H_2.$$

Since the decomposition of the steam according to the second reaction is endothermic, it was found that the coke charge cooled more rapidly than heat could be imparted to it through the fireclay walls of the generator. This resulted in the formation of carbon dioxide in such quantities that the process was rendered uneconomical.

In 1849 Gillard introduced a process which embodied the idea of raising the temperature of the carbonaceous fuel by blowing air through it instead of heating it externally. In this way the fuel was raised to incandescence by its own partial combustion. The air supply was then shut off and steam passed through the hot fuel bed until the temperature fell to such an extent that a fresh air blast was necessary. It is this principle of alternate "blow" and "run" which has since become normal practice. This important development by Gillard was followed by numerous other attempts to introduce water gas on a commercial scale. It was not until 1873, however, when Lowe erected a carburetted water-gas plant at Phœnixville, in the United States, that the industrial production became established practice.

The fact that water gas contains over 90% combustible gases, as compared with about 30% in producer gas, soon attracted attention to its value for welding purposes, and in the early "eighties" plant was erected in this country and elsewhere to supply water gas for welding tubular boilers and for other work of a like character. An apparatus installed at the Leeds Forge in 1887 was typical of the kind of plant then employed. The generator consisted of a cupola furnace about 20 ft. in height and 7 ft. in diameter, lined with firebrick, with a constriction a short distance above the hearth, the firebrick being protected at this point by a water-cooled ring. An air blast was admitted below this ring and, in about 10 minutes, the ignited fuel was raised to incandescence. The air blast was then cut off, steam was admitted above the top of the fuel and, passing down through it, became converted into water gas which was led away through the same opening as that through which the air blast was admitted, this being opened and closed by means of a water-cooled slide valve of such construction that it was impossible for any explosive mixture of water gas and air to be formed. The water gas passed on to purifiers for the removal of hydrogen sulphide and carbon dioxide, and the gas was then stored in holders. The fuel was fed into the generator from the top, which was closed by a cone and the pipe systems for steam, air and water gas were controlled by an arrangement of lever valves which rendered any formation of explosive mixture impossible.

Conditions of manufacture at this period still prevented rapid progress in the utilisation of blue water-gas. It has already been stated that the reaction between the steam and the carbon to produce water gas is an endothermic one, the heat absorbed in the reaction being made good by the intervening " blow " period, whereby the fuel is again raised to incandescence. Theoretically, it should be possible to obtain the required heat balance by burning half the fuel by an air blast to producer gas and converting the remaining half to water gas by the steam reaction. In practice, however, the loss of heat due to the escape of hot producer-gas and by radiation, etc., made it necessary to continue the air blast until a much greater proportion of the carbon in the fuel was consumed.

Had it been possible in the early days to recover the producer gas and burn it whilst hot for any purpose, the efficiency of the process would have been greatly increased and there can be little doubt that more rapid progress would have been made. Since the producer gas is about 4 times the volume of water gas made, and as the gases are produced intermittently, the difficulty of utilising both appeared almost insurmountable.

When the manufacture of carburetted water gas was first successfully carried out, it became apparent that the producer gas, the loss of which had crippled all water-gas processes, could be utilised for heating chambers filled with chequer brickwork to the temperature required for the thermal decomposition of the oil to gaseous products. The oil gas thus obtained was mixed with the blue water-gas to give the now familiar carburetted water-gas. The producer gas formed during the period of raising the fuel to incandescence was at once burnt, with a minimum loss of sensible heat, in the superheating chambers. In this way the efficiency of the process was greatly improved.

The increase in the price of cannel coal towards the end of last century directed the attention of the gas industry in this country to the use of carburetted water-gas for raising the illuminating power of coal gas. Its use in this respect has now ceased to be significant, but its value in other respects has given the carburetted water-gas process an important position in the present-day production of town's gas. The process was adopted by the Gas Light and Coke Company at Beckton in 1890, and is now extensively used as an auxiliary to coal-gas manufacture. Many improvements designed to improve the efficiency of production and to reduce the cost of manufacture have been effected in recent years, *e.g.* the development of waste-heat boilers, the use of self-clinkering grates, the back-run process, etc. They have contributed in no small measure to the high efficiency of a modern plant as typified by that of Messrs. Humphreys and Glasgow.

Just as the successful operation of a carburetted water-gas plant depends upon raising the thermal efficiency of the process by recovery of the heat energy in the producer or blow gases, so also does that of the blue water-gas process. In a modern plant steam required for gas making is generated and may be superheated, and a surplus of steam is usually available for general process work. Another factor in the economy of the blue water-gas process is plant size. It is only in water-gas plant of large size that it becomes a commercial success to employ refinements in design that will give the highest efficiency from a thermal as well as an operating point of view (*cf.* N. E. Rambush, Proc. Internat. Conf. Bit. Coal, 1931, **1**, 840).

A modern plant for the production of blue water gas consists of the following main parts:

(1) the gas generator,
(2) the valve control mechanism,
(3) apparatus for the recovery and utilisation of waste heat, and
(4) the gas cleaning plant.

THE GAS GENERATOR.—The interior walls of early generators were constructed of firebrick throughout, but with increase in generator capacity, trouble was experienced due to fusion of clinker with the bricks of the lining. This adhered so tenaciously to the sides of the generator that the rate of gas production was seriously limited. Water jacketing of the lower part of the generator casing was therefore adopted and is now general practice on large installations. The steam developed in the jacket is used for gas making, and for this reason it is usual to operate the jacket at a working pressure approximating to that at which the steam is admitted to the generator. It should be noted that in practice the effect of the water jacket is to lower the fuel-bed temperature with a corresponding lowering of the rates for the gas reactions. Because of this cooling effect, jacketed generators are not economical at low production rates.

As accessories to the generator, means are provided for the supply of fuel under gas-tight conditions and for the removal of ash and clinker. The fuel bed must be maintained at the same density throughout, in order that the steam and air may spread evenly over the whole area. A mechanical fuel-feeding device of the cyclic or of the continuous type is essential if a gas of constant composition is required. Such devices have the additional advantage that gas making need not be interrupted to enable the generator to be charged. Experience has shown that there are two causes for the variation in gas quality which is inherent in a system employing a static feed. Firstly, the fuel depth and thus the fuel-bed resistance gradually decreases after charging and, secondly, the top of the fuel bed undergoes wide temperature fluctuations with each charging of cold fuel on to the hot bed.

The high gas-pressures used on water-gas generators and the intermittency of gas making necessitate mechanical fuel-feed designs differing from those used on gas producers. In the cyclic charger the fuel is admitted as a bulk charge into the generator once per cycle. Operation may be governed directly from an automatic valve-controlling machine, so that the coke is admitted to the generator fuel-bed at one predetermined point in the cycle, namely, during the down- or back-run, when the top of the generator is free from combustible or toxic gases.

In the continuous charger, coke is continuously and regularly fed on to the fuel bed, a revolving steel distributor in the top of the generator spreading the coke from a gas-tight hopper evenly over the bed. Provision is made for the automatic recharging of the hopper under gas-tight conditions when required.

It is of the greatest importance that the fuel bed should be of the correct depth, a factor which must be considered in conjunction with the type of fuel to be gasified and also in relation to fuel-bed resistance, pressure of air and steam, duration of " blow " and velocity of gases.

Ash and clinker are removed continuously from the base of the generator by mechanical means. Neglect in this direction results in a reduction in the quality and quantity of gas produced and adversely affects thermal efficiency. In addition, excessive quantities of unburnt fuel may be lost in the ashes. Grate designs used in water-gas generators are based on those used successfully for many years with producer-gas generators. The ash-removing mechanisms are thus of the two types known as " wet base " and " dry base." With the wet grate the base of the generator is sealed in a water pan. This type is the more accessible, but it is difficult to accommodate the blast pressure used in the generator. For this reason a dry base, which involves a totally enclosed generator, is normally used in blue water-gas manufacture, since the generators must be operated at high blast-pressures in order to obtain the highest possible yield of gas from a given quantity of coke. The operation of a grate of this type is described below. A wet base finds satisfactory application in carburetted water-gas practice.

Valve Control.—All large water-gas units are now fitted with mechanically timed and controlled valves. These modern controlling devices have proved highly satisfactory in operation, though their mechanism is, of necessity, intricate and the service conditions exacting. The valves must be capable of withstanding exposure to sulphur compounds, abrasive dust and reducing gases, in addition to wide fluctuations of temperature. The automatic control, which is commonly operated by hydraulic or mechanical power, ensures that during a cycle the valves are opened and closed in a correct sequence and at the right intervals. The mechanism provides for audible warning in the event of interference with the predetermined cycle.

Heat Recovery.—As has been indicated already, the recovery and utilisation of the sensible and potential heat in the blow gases and the sensible heat of the water gas leaving the generator is important. It is necessary at this point to make a clear distinction between a blue water-gas plant and one for the manufacture of carburetted water-gas. In the latter sufficient heat is required from the blow gases to operate the carburettor and superheater in a satisfactory manner. In a blue water-gas plant, on the other hand, the gas-making process is complete when the gases leave the fuel bed and it is desirable that as little potential heat as possible should leave the generator in the blow gases. In fact the opinion has been expressed (N. E. Rambush, *l.c.*) that a higher gasification efficiency for blue water-gas units can be obtained only if future generators are so designed and operated that the amount of potential heat in the waste gas becomes of so small an order that only the sensible heat thereof is worth recovering.

A low content of carbon monoxide in the blow gas can be attained by the use of a relatively high air-rate, by reduction of the depth of the fuel bed and by reducing the air-steam ratio.

Heat recovery may be effected by means of a heat-exchange apparatus of the recuperator type. This is essentially a brick-lined vessel with inlet and outlet for the gases and suitable arrangements for admitting secondary air to burn *in situ* any carbon monoxide in the blow gases. These gases then pass to the waste-heat boiler where sensible heat is extracted from them in the generation of steam. The steam thus produced may be led to the recuperator tubes where it is superheated. During the passage of the blow gases the stack valve is in the open position so that the gases pass from the waste-heat boiler to the atmosphere. This valve is closed to the water gas which is diverted to the cleaning plant.

Clean-cut division between the blow gases and the water gas leaving the waste-heat boiler is not possible. It generally happens that eddying and diffusion result in the production of mixed fractions at the beginning and the end of the water-gas run. On works where the water gas is manufactured as a source of hydrogen for different processes these two mixed fractions may be separately treated.

The Gas Cleaning Plant.—The gases leaving the generator contain dust, in addition to sulphur compounds and water. This is liable to deposit in valves and mains, and even its dispersal into the atmosphere with the blow gases leaving the stack may be objectionable. Arrangements are accordingly made to obviate such trouble and may include water lutes, into which the dust from the valves and other parts of the plant is expelled mechanically, by pressure jet or by hand.

The water gas must be subjected to further cleaning after it leaves the waste-heat boiler. The degree to which this cleaning is carried out will depend upon the purity required, but the treatment normally includes passage through a washer cooler in which the gas is washed by cold water in countercurrent. The gas leaving the washer still contains a little dust and some tarry matter and the complete elimination of these impurities entails the use of additional plant, *e.g.* centrifugal cleaners in which the gas is intimately mixed with water or other suitable fluid.

The presence of sulphur compounds in water gas is very undesirable for some purposes. Only a part of the sulphur is eliminated in the water wash and it may be necessary to pass the gas through iron oxide as for the removal of hydrogen sulphide in the manufacture of town's gas, and then through a catalytic process for the removal of organic sulphur compounds.

Operation of the Plant.—The operation of a blue water-gas plant may be well illustrated

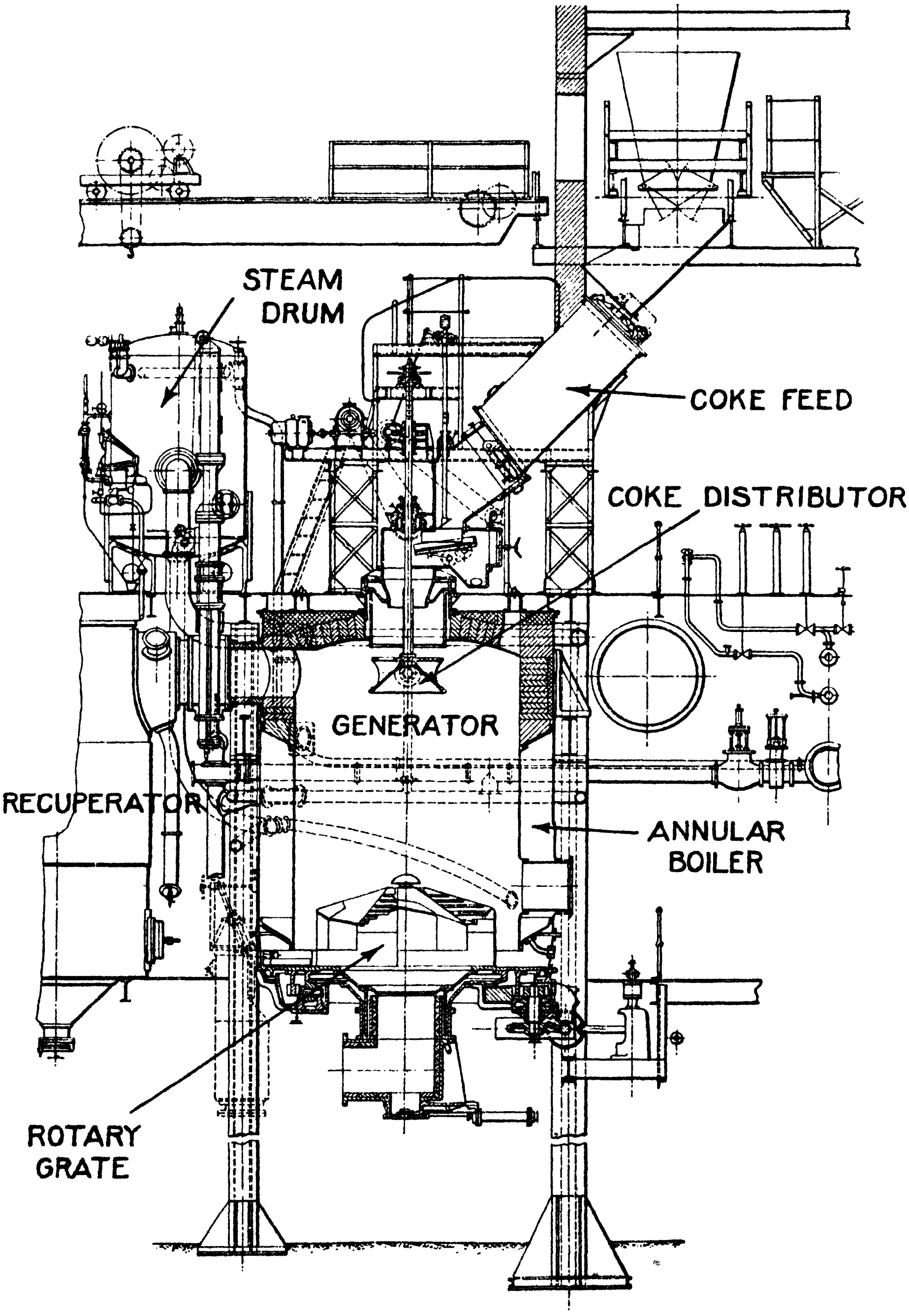


Fig. 1.

by reference to a Power Gas Corporation plant (Fig. 1), as installed at Billingham, of which a full description has been given (Engineering, 1929, **127**, 348, 450, 508). The cycle consists of five stages (Fig. 2). In the blow stage, air is passed up through the fuel for a period of about 1 minute, and is thence conducted through recuperators and waste-heat boilers to the

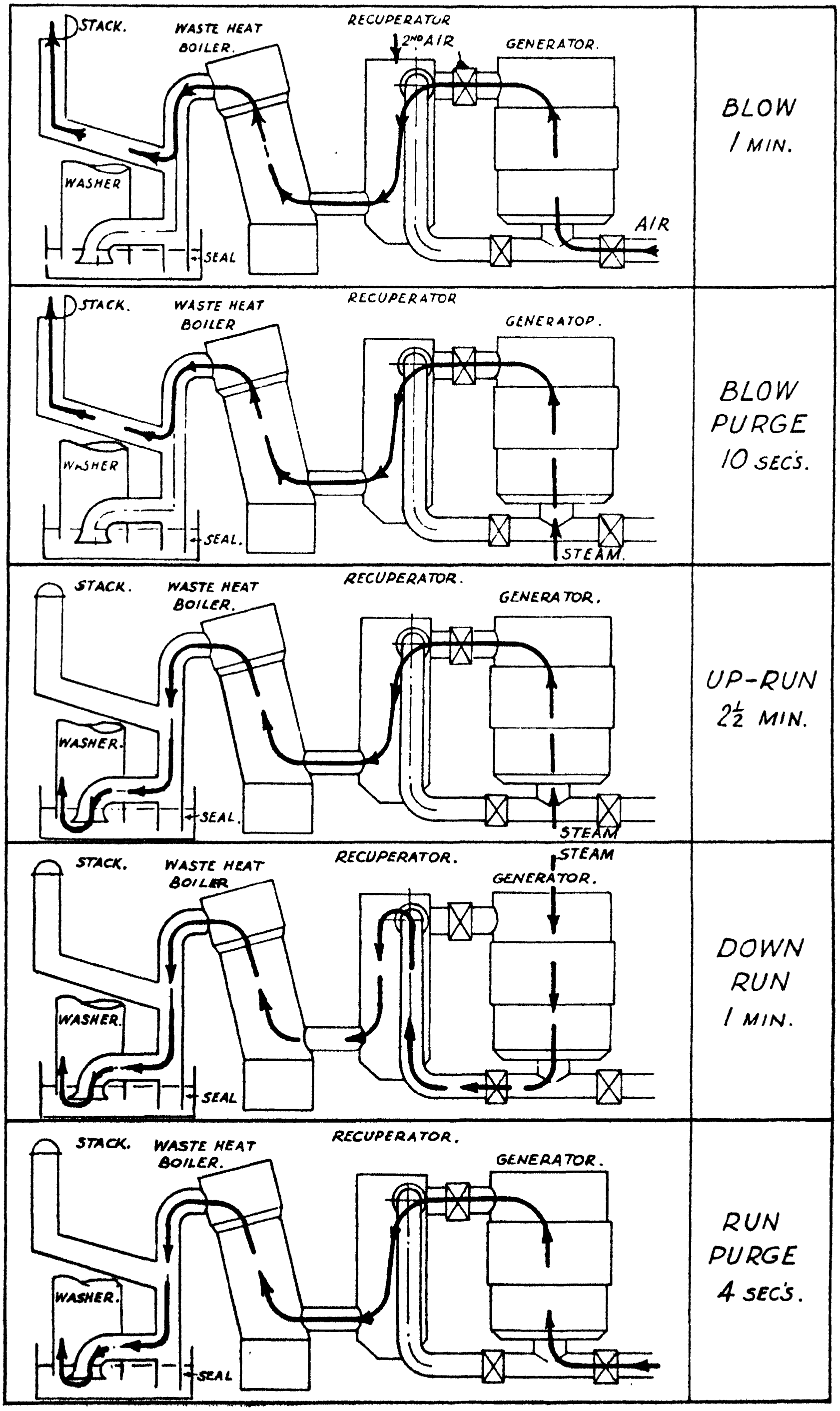

STACK.
WASTE HEAT BOILER.
RECUPERATOR
2ND AIR
GENERATOR.
WASHER
SEAL
AIR
BLOW
1 MIN.
STACK.
WASTE HEAT BOILER
RECUPERATOR
GENERATOR.
WASHER
SEAL.
STEAM.
BLOW
PURGE
10 SECS.
STACK.
WASTE HEAT BOILER.
RECUPERATOR.
GENERATOR.
WASHER.
SEAL.
STEAM
UP-RUN
2½ MIN.
STACK.
WASTE HEAT BOILER
RECUPERATOR.
STEAM
GENERATOR.
WASHER.
SEAL
DOWN
RUN
1 MIN.
STACK.
WASTE HEAT BOILER.
RECUPERATOR.
GENERATOR.
WASHER.
SEAL
RUN
PURGE
4 SECS.

FIG. 2.

atmosphere. Air is then cut off and steam passed up through the fuel for about 10 seconds, during which time the gas formed, mixed with air remaining from the blow stage, is permitted to escape to the atmosphere, this stage being known as the blow purge. In the next or "up-run" stage the outlet to atmosphere is closed and the steam supply continued, the pure water gas formed being led to the gas collecting main. The up-run continues for about 2½ minutes, during which time the temperature of the fuel, especially that in the lower portion of the bed, falls. The upper part of the fuel bed, however, remains sufficiently hot for gas making, so that the direction of flow of the steam is reversed for the next, or "down-run" stage, which is continued for about a minute, the steam then entering at the top of the generator and the gas leaving from the bottom. Finally, air is passed upwards through the fuel for a few seconds to drive out the gas remaining in the generator and its connections into the collecting main, the stage being known as the "run purge." These five stages are continued, under automatic control, for the whole time that the plant is in operation.

Screened coke from an overhead bunker is supplied to the generator through a gas-tight receiving chamber with valves at its upper and lower ends, the coke being delivered to this chamber in bulk and passing from it slowly and continuously on to a rotating cast-steel distributor in the form of a combined plate and cone, which distributes the coke evenly over the fuel bed. The feeding of coke to the generator presents difficulties greater than are met with in producer-gas practice, because the working pressures are higher, and also because loss of water gas due to leakage represents a relatively greater thermal loss per unit volume.

The generator itself is water-jacketed in the lower portion. The steam from the jacket is led to a steam drum, from which it is fed to the generator for gas making. The upper portion of the sides of the generator are lined with firebrick and above the top plate is a water jacket in the form of a shallow tank, the object of which is to prevent heat radiation to the operating platform above. The exterior of the generator is faced with insulating brickwork.

The fuel is carried on a mechanical iron grate having renewable conical plates of hardened steel on the faces subjected to wear. This steam-driven grate slowly rotates and, at the same time, the curved upper surfaces raise and lower the fuel bed, thereby maintaining a uniform density throughout. The conical formation of the grate also tends to move the lower strata of fuel from the centre to the sides, where it falls and is crushed between the sides of the grate and the generator wall. In this way the clinker is steadily removed from the fuel bed and broken up to a size suitable for removal. The revolving table on which the grate is mounted also carries the crushed clinker to the ash boxes, where it is swept in by means of adjustable ploughs. It is desirable that the ashes should not be removed too rapidly, since a sufficient quantity should be left round and above the grate to protect it from the heat. For this reason the extraction rate can be regulated by adjusting the speed of rotation and the position of the ploughs or by working the grate intermittently. The fuel bed can be tested periodically for ash and clinker by means of plugged pokeholes, provided through the wall of the generator for this purpose.

Air for the blow is led by way of a control valve through the bottom of the generator to the grate and so to the fuel bed. The air is provided by air blowers driven by low-pressure steam turbines. The blow products leave the generator at the top, from which they pass to the recuperator and thence through the waste-heat boilers to the stack.

The steam for the up-run enters the generator through the air passage. For the down-run it passes in by way of a side connection near the top of the generator. The water gas produced in both runs is led to the recuperator. The flow of air, steam and gas is entirely controlled by hydraulically-operated valves.

The automatic control machine is so designed that the plant can be operated by hand if required. The automatic operation opens and closes the main valves in their correct order and stops gas making if any do not open or complete their stroke, or if they operate in any other irregular manner. Audible and visible warning is then given. When the automatic control machine stops the plant, it returns the valves to a safe position and, at the same time, stops itself in a safe position for restarting. It also indicates the position in which the valve should be at any moment, as well as their actual position. If resort is made to hand operation, the operating handles are interlocked to make irregular working impossible. These automatic control machines are capable of controlling a number of water-gas units, and when so doing they can keep all the units operating in synchronised cycles, suitably out of phase, in order to smooth out the load on the blowers and purification plant.

The recuperator consists of a cylindrical shell lined throughout with brickwork and provided with inlet and outlet for gases at top and bottom. The gas produced in the up-run passes in through the same inlet as the blow gases, but a separate and smaller inlet is provided at the top of the vessel for that made on the down-run. Secondary air is supplied to the blow gases by an annular passage surrounding the gas inlet, entering the latter through holes provided for the purpose. The superheater tubes are of U shape surrounded with fireclay tubes and are thus protected from direct contact with the gases.

The waste-heat boiler employed is of the fire-tube type. It is slightly inclined from the vertical and the hot gases from the recuperator enter by way of a distributing chamber at the bottom. After passing up through the fire tubes, the gases collect in a similar chamber at the top and from there they pass to the stack, or, in the case of the water gas, to the washer. In other installations a horizontal fire-tube type of boiler has been preferred.

A Lymn washer such as is used for cleaning and cooling the gas is shown diagrammatically in Fig. 3. It consists of a cylindrical steel vessel open at the bottom, which dips into water in a concrete tank, thereby forming a seal. A water inlet connection is provided at the top and the gas from the waste-heat boiler enters at the bottom through the curved pipe shown on the right of the diagram. The bottom mouth of this pipe is serrated and dips below the water in the seal, which is sufficiently deep to prevent the passage of waste gases into the washer or the escape of water gas from it when the stack valve is open. A series of conical discs and rings is provided in the casing, the rings being attached to the walls of the washer and the discs carried by a central shaft. As the gas ascends the washer it passes through the water trickling over the edges of the discs and rings and is thereby effectively cooled and freed from dust. The dust carried down by the water collects in the concrete tank and is removed manually at intervals. In addition, some dust from the gas falls directly into the water from the sealed inlet pipe leading to the washer.

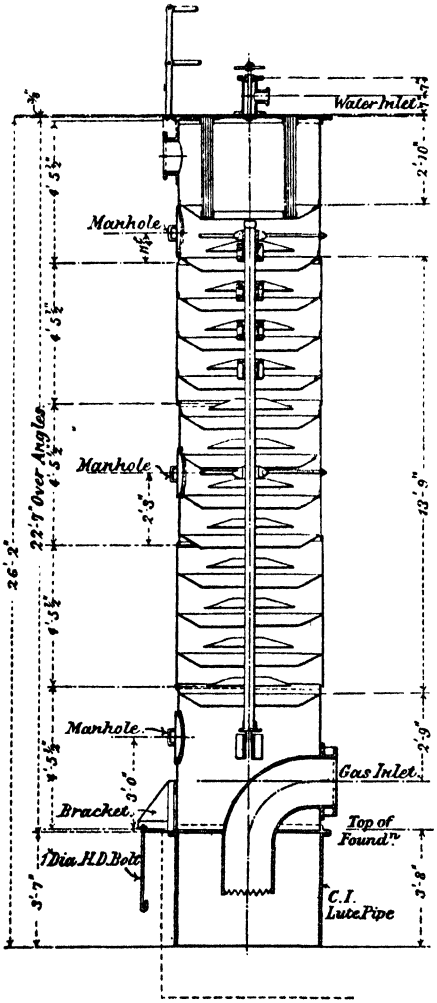


Fig. 3.

Chemical Reactions in Blue Water-Gas Production.

It has already been explained that water gas is made by the interaction of steam with coke or other carbonaceous fuel which has previously been heated to reaction temperature by means of an air blast. The chemical reactions involved will be dealt with briefly, but for greater detail H. Hollings and R. H. Griffith, "Water Gas," 1934, p. 6, should be consulted.

The products of the interaction of steam and coke may be regarded as being derived from a combination of the two reactions:

(i) $C+H_2O$ (Steam) $=CO+H_2-52{,}590$ B.Th.U. per lb.-atom.

(ii) $C+2H_2O$ (Steam) $=CO_2+2H_2-33{,}170$ B.Th.U. per lb.-atom.

The formation of hydrogen and carbon dioxide occurs at lower temperatures, but it requires more steam and absorbs less heat from the generator. It is interesting to note that both reactions produce 2 lb. mol. of combustible gas from 1 lb. atom of carbon, and since the calorific values of carbon monoxide and hydrogen are almost equal, it follows that a therm of blue water gas requires approximately the same carbon (4·86 lb.), no matter by what reaction it may be produced. Generally speaking, a high carbon dioxide content is objectionable on account of lowering the calorific value of the water gas, but for purposes where a high hydrogen content is required in the finished gas it may be desirable, since the associated carbon dioxide can be removed by washing under pressure. The rate of reaction is, however, greater at the higher temperatures necessary for the first reaction.

Technically equilibrium is not attained owing to the rapid rates of steam supply, large quantities of steam escaping decomposition. It would be expected that this would seriously disturb the reversible water gas reaction,

$$CO+H_2O \rightleftharpoons CO_2+H_2,$$

but, in practice, the carbon dioxide content is much lower than that which would be in equilibrium with the undecomposed steam present. By whatever mechanism the blue water-gas is produced, it is known that a hot fuel bed leads to a high steam-decomposition and a low carbon dioxide content in the water gas.

Water gas may contain a number of impurities originating from the coke substance, such as hydrogen sulphide, carbon disulphide and nitrogen, as well as residual blow gas left in the vessels. The amount of blow gas to be accepted varies according to circumstances, *e.g.* a blue water-gas plant making gas intended for hydrogen production limits its nitrogen content below 2%, but if the hydrogen is to be used for ammonia synthesis, high proportions of nitrogen can be accepted. Similarly, in American practice blow gas may be deliberately mixed with the carburetted water-gas because local ratios of oil and coke prices encourage this procedure. Methane also occurs in water gas and its presence has been attributed to residual volatile matter in the coke, synthesis from carbon monoxide and hydrogen or from coke and steam. A typical water gas analysis is:

CO_2.	CO.	H_2.	CH_4.	N_2.
5·0	40·0	51·0	0·3	3·7

As steaming progresses, the fuel bed is cooled and the carbon dioxide and undecomposed steam contents increase. At the same time the rate of gas production becomes uneconomic as shown diagrammatically in Fig. 4. Heat must again be stored in the fuel bed by means of a blast.

During the blast the products of the reaction, after passing through the first shallow layer of the active fuel bed, are derived from the reaction:

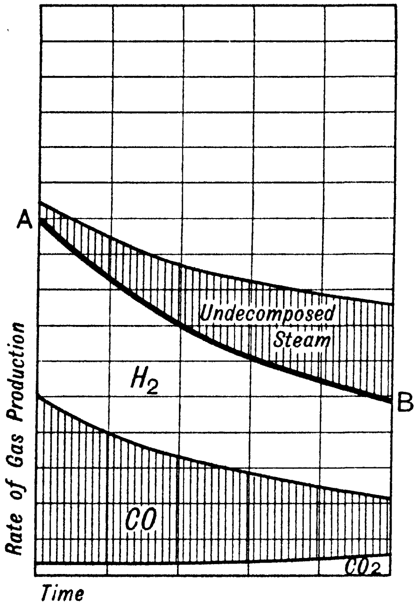


FIG. 4.

$$C+O_2(+4N_2) \rightarrow CO_2(+4N_2)+172{,}560$$
B.Th.U. per lb.-atom.

From the point of view of heat storage in the generator it would be ideal if it remained at this stage, but further reduction to carbon monoxide can occur by the reaction:

$$C+CO_2(+4N_2)=2CO+(4N_2)-72{,}000$$
B.Th.U. per lb.-atom.

which consumes more carbon and absorbs heat which was intended for water-gas production.

Higher rates of blasting decrease the extent of this reduction, and this fact is one of the reasons why higher blast pressures are favoured in blue water-gas plant as distinct from carburetted water-gas plant where there is an opportunity of utilising the potential heat of the blow gases.

As the temperature of the fuel bed rises, the production of carbon monoxide is accelerated (Fig. 5). This involves the disadvantage of increased thermal loss, but it makes for high rates of production of blue water-gas of high quality. If high outputs are not required, the inconsistency may be avoided because the rate of steaming can be very low compared with the blast (*cf.* Fuel Research Board Tech. Paper No. 43). Under these conditions the fire remains cool and therefore the carbon monoxide content in the blow gas is kept low, but the water-gas calorific value is maintained because of the low rates of steaming. Such a method of operation is not commercially feasible because of the high capital charges involved.

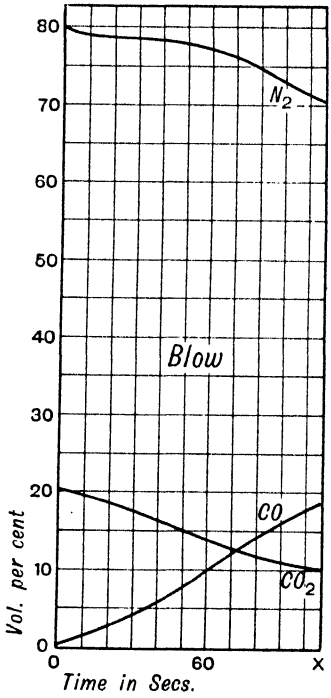


FIG. 5.

As blowing proceeds and the temperature of the fire rises the proportion of carbon monoxide rapidly increases. The combustion of the blow gas in recuperators (in blue water-gas sets) or carburettors (in carburetted water-gas sets) has been greatly improved in some recent installations. In those generators fitted with annular boilers the blow gas at the periphery is poorer in carbon monoxide content than that at the centre and this stratification persists through the second vessel. For this reason the former mode of secondary air admission at the shell of the second vessel led to poor mixing, uncertain ignition and incomplete combustion. The method now adopted for overcoming this consists in the introduction of secondary air at the generator-carburettor connecting main where velocities are high and good mixing results.

Furthermore, the rate of secondary air admission is controlled by a "creeper" cam which is shaped to correspond with the increasing carbon monoxide content of the blow gas. In this way the blow gas can be perfectly burnt and the heat made available for steam raising, oil cracking or interchange with back-run steam. When sufficient heat has been stored in the fuel bed, the blow is ended and the blow gases expelled from the plant by the water gas in the purge which follows.

Air–Steam Ratio.—F. J. Dent, who has carried out extensive water-gas trials on behalf of the Joint Research Committee of the Institution of Gas Engineers and Leeds University, has introduced a useful conception—the "air–steam ratio," which may be defined as the ratio of the cubic feet of air supplied to the fuel bed during the blow to the pounds of steam passing through the fuel bed during steaming. The air–steam ratio is a fundamental factor governing the temperature of the fuel bed and the reactions occurring in it. It determines the composition of the blue water-gas produced and the carbon monoxide concentration of the blow gas. Related to the potential heat in the blow gas is the fuel consumption and the heat available for steam raising. With air–steam ratios lower than 30 the carbon dioxide in the blue water-gas increases beyond an economic limit. The degree of dependence upon outside steam may be another limiting factor. With air–steam ratios greater than 70 the output falls to a prohibitive point, coke consumption rises, steam is over-abundantly available and clinker formation is liable to disturb the fuel bed conditions.

The influence of the air–steam ratio on the compositions of the water gas and blow gas is shown in Fig. 6. The graph also indicates the fall in output and increasing steam decomposition which result from increase in air–steam ratio. The fall in yield of water gas per 1,000 lb. of coke due to the increased potential heat in the blow gas can also be seen. The graph should be studied in conjunction with Fig. 7, showing the influence of air–steam ratio on the rates of steam supplied for gas making and for ancillary plant as well as the rates of steam generation from the annular and waste-heat boilers. Self-sufficiency in steam occurs at an air–steam ratio of about 40. These results, extracted from F. J. Dent's data (Trans. Inst. Gas. Eng. 1935–36, **85**, 276) refer to a Humphreys and Glasgow generator of 8 ft. 8 in. internal diameter.

The influence of the air–steam ratio upon the carbon distribution per therm. of B.W.G. made is as follows:

Air–steam ratio . .	72	52	32
Total carbon supplied .	14·01	11·78	10·39
Carbon burnt during blow	8·21	6·21	5·02
Carbon occurring in B.W.G.	4·86	4·86	4·86
Carbon in ashes, clinker fliers	0·94	0·71	0·51
Total carbon in products	14·01	11·78	10·39

and the corresponding thermal balances are affected in the following manner:

Heat absorption (therms per therm B.W.G.):			
By reaction between carbon and steam .	0·211	0·208	0·203
As sensible heat in B.W.G.	0·060	0·055	0·052
As sensible heat in undecomposed steam .	0·018	0·022	0·037
By generator boiler .	0·122	0·103	0·101
By evaporation of moisture in coke .	0·010	0·010	0·010
By radiation convection (and by water seals)	0·016	0·015	0·015
	0·437	0·413	0·418
Heat returned to generator by back-run steam	0·024	0·030	0·050
Heat production:			
Potential heat in blow gas	0·572	0·356	0·228
Sensible heat in blow gas	0·221	0·172	0·140
Sensible heat stored in the fuel bed. . .	0·413	0·383	0·368

Other Variable Factors.—Apart from alteration in the air–steam ratio, the number of other factors which may be varied is considerable, *e.g.*:

(i) The length of the cycle.
(ii) The proportion of time occupied by the blow.
(iii) The proportion of steam used on the down-run or back-run.
(iv) The pressure of the air blast.
(v) The depth of fuel bed.
(vi) The nature of the fuel.

The operation of a water-gas plant is complicated by the large number of variable factors involved, but by a correct appreciation of these factors a water-gas plant can be made a highly flexible machine capable of wide variations in output, gas quality and steam production when using a range of fuels varying in size and moisture content.

(i) *The Length of the Cycle.*—This should be as short as mechanical limitations will permit. The shorter the cycle the smaller is the cyclic fluctuation in the temperature of the fuel bed. The later part of the "run," which is associated with a high content of carbon dioxide, low steam decomposition and low output, is eliminated. With hand-operated sets it was difficult to reduce the cycle below about 5 minutes, but now, with fully automatically-operated valves of refined design, the cycle can be reduced to about 2 minutes 40 seconds. Further reduction is limited by the fact that the purging of blow gas by blue water-gas and *vice versa* does not involve a perfect separation and, to avoid excessive loss of blue water-gas, some blow gas has to be accepted. The amount of blow gas

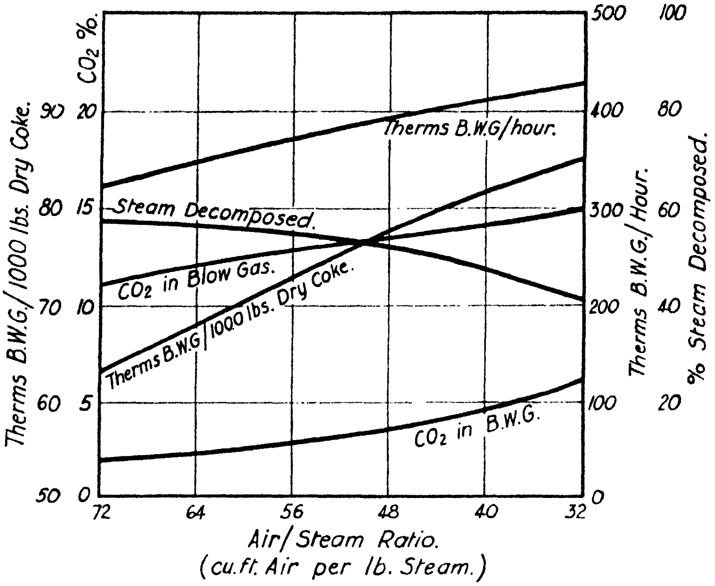

Therms B.W.G./1000 lbs. Dry Coke.
CO2 %.
90 20
80 15
70 10
60 5
50 0
500 100
400 80
300 60
200 40
100 20
0
Therms B.W.G./Hour.
% Steam Decomposed.
Therms B.W.G/hour.
Steam Decomposed.
CO2 in Blow Gas.
Therms B.W.G/1000 lbs. Dry Coke.
CO2 in B.W.G.
72 64 56 48 40 32
Air/Steam Ratio.
(cu.ft. Air per lb. Steam.)

Fig. 6.

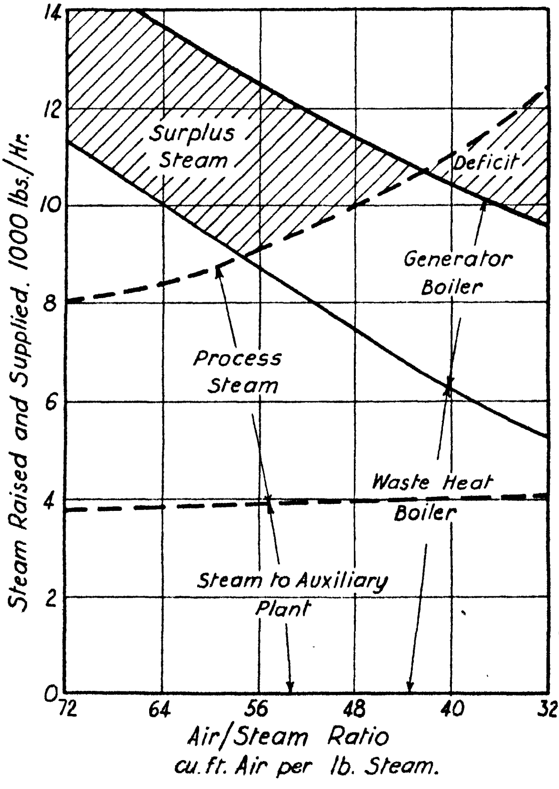

Steam Raised and Supplied. 1000 lbs./Hr.
14
12
10
8
6
4
2
0
Surplus Steam
Deficit
Generator Boiler
Process Steam
Waste Heat Boiler
Steam to Auxiliary Plant
72 64 56 48 40 32
Air/Steam Ratio
cu.ft. Air per lb. Steam.

Fig. 7.

to be accepted and the amount of blue water-gas to be lost is a constant quantity per cycle and becomes an excessive proportion with short cycles. Similarly the amount of steam wasted by being left in the carburettor and superheater at the conclusion of the back-run is constant and its proportion increases with shorter cycles. The back- or down-run is followed by a second short up-run as a safety precaution to prevent air blast coming into contact with combustible gas at the base of the generator. This short up-run represents lost time and lost steam and remains constant for all lengths of cycles. Valve changes also occupy an appreciable time and wear and tear on the valves is dependent on the frequency of their use.

(ii) *The Proportion of Time Occupied by the Blow.*—The output of blue water-gas is dependent on the heat stored in the generator to meet the endothermic requirements of water-gas production. This, in turn, depends upon the blow period if the blasting rate is constant. The function of a water-gas plant in the gas industry in meeting peak loads stresses the importance of high outputs. With long blow-periods the rate of steam supply has to be correspondingly increased and this causes a lower steam decomposition and a poorer quality of blue water-gas. The efficiency of blue water-gas production falls, and if the gas is to be carburetted, the shorter time for oil injection adversely affects oil-cracking efficiency. The upper limit of blow period is about 48%, but for low outputs the blow period can be reduced, although for very low outputs it would probably be better to operate discontinuously.

The influence of the length of the blow period upon output, thermal yields and steam decomposition is shown in Fig. 8 (*ibid.* 1935–36, 287). Decrease in the blow period reduces the output but the thermal yield is improved. The steam decomposition does not increase because in this case the plant was operated with a constant carbon dioxide content in the water gas for all the different blow periods. This involved a decrease of air–steam ratio superimposed upon the reduction in blow period. Had the air–steam ratio been constant, the improvement in thermal yield would not have been as great and the steam decomposition would have been increased as the blow period was reduced. The corresponding steam balance is shown diagrammatically in Fig. 9.

(iii) *The Proportion of Steam Supplied on Down-Run or Back-Run.*—The proportioning of up and down steaming is related to the control of clinker formation and its extraction by hand or by mechanical grates. The maintenance of good fire conditions is not as amenable to scientific control as the other factors affecting water-gas production, and considerable reliance has to be placed on the skill and experience of the gas maker.

Control aims at preventing the solidification of the molten ash at a higher level than that at which it can be extracted. Bridging over of large masses of clinker above the zone affected by the crushing mechanism of the grate would lead to "channelling" and loss of output. Solidification at too low a level, *e.g.* on the grate itself, would lead to clogging of the grate bars, bad distribution of air and steam and damage to the grate.

The fuel bed in the generator can be regarded as being comprised of three zones—a lower zone (about 3 ft.) of ash and clinker, the depth of which is determined by the speed of the grate, a middle zone (about 2 ft.) of higher temperatures where the chemical reactions are predominant, and an upper zone (about 3 ft.) of coke which is too low in temperature for reaction because coke recently added has not had the opportunity to warm up to the temperature of the rest of the fuel bed.

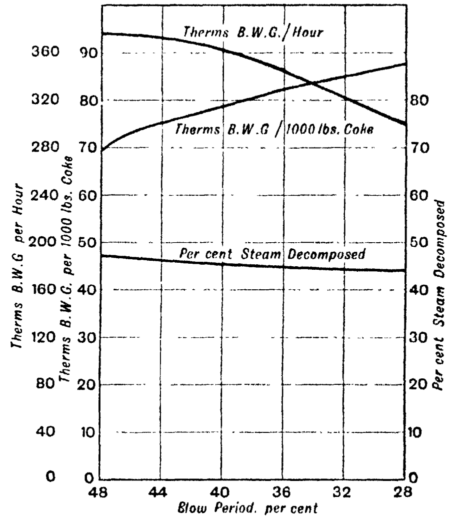


FIG. 8.

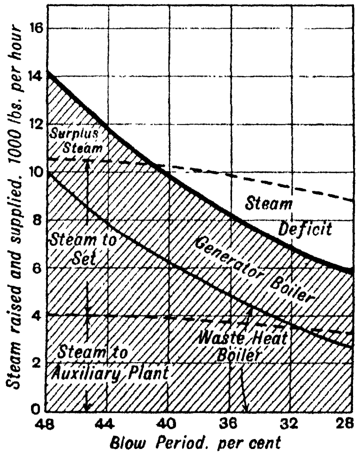


FIG. 9.

The top and bottom layers serve important functions as heat regenerators. Without a down-run or back-run, the hot zone would rise because the air blast and steam would reach the hot zone with little preheating and thus lead to a cooling of the first part of the reaction zone. The sensible heat of the blow gas and blue water-gas, however, would be partially transferred to the top zone which would become progressively hotter. With a down-run, however, heat is transferred from the top layers, thereby preheating the down-run steam before it enters the reaction zone. Furthermore, the sensible heat of the down-run water gas is interchanged with the clinker zone. The heat so stored in the clinker is transferred to the blast and up-run steam. The amount of down- or back-run steam has, therefore, an important influence on the position of the hot zone and upon the position of clinker formation.

Back-run steam is more advantageous than down-run steam because it may be preheated to 700° before entering the generator. This useful heat returned to the generator makes it advisable to use as much back-run steam as possible, particularly since it also leads to a reduction in the temperatures of the blow gas, blue gas and undecomposed steam leaving the generator and consequently to a higher thermal efficiency.

Unfavourable clinker formation is watched by periodic exploration of the fire by testing the ease of penetration of the fuel bed with rods, and occasionally a rod may be left in for a few minutes and when withdrawn, the location of bright red, red and black sections on the rod indicates the zoning in the fire. The grate is examined from below to detect the formation of clinker on the bars or the overheating of the grate. An ammeter indicates excessive load on the motor driving the grate, whilst pyrometers fitted to the crushing stools or some other arbitrary part of the grate and a back-run-gas pyrometer assist in maintaining good fuel-bed conditions. The Fuel Research Board (Technical Paper No. 43) have made a study of the factors leading to clinker formation.

The annular boiler, which is usually installed with a mechanical grate, may raise 35 lb. of steam per 1,000 cu. ft. of water gas, and it is customary to operate these boilers at about 35 lb. pressure and employ the steam produced for process purposes, but water-tube boilers can also be fitted to generators and work up to 350 lb. per sq. in. The annular boiler derives its heat partly from that which would otherwise be lost by radiation, partly from the sensible heat of the gases, but also by conduction from hot coke in the generator. The extent to which this conduction occurs is difficult to assess and a simple comparison with a brick-lined generator is not possible because of complication by other variables.

(iv) *The Pressure of the Air Blast.*—The advantage of raising the blast pressure is particularly great in the production of blue water-gas when there is smaller use for the potential heat of the blow gas. Water-gas plant is commonly operated at a blast pressure of about 22 in. w.g., but recent plant have employed pressures as high as 50 in. and this, in fact, is common practice in America. This high pressure necessitates deepening the wet seals on the generator or, more usually, adopting a dry grate.

Increasing the blast pressure involves a shorter time contact and less loss in the form of carbon monoxide in the blow gas. This increases the heat stored in the fuel bed and hence the thermal efficiency of blue water-gas production, but it lowers the waste-heat steam generated. The proportion of the cycle occupied by the blow is reduced and the plant output increased. Limits to the blast pressure are set by the loss of coke blown from the fire and the increased difficulty due to clinker formation.

J. G. King and B. H. Williams (F.R.B. Tech. Paper No. 43) have also studied the effect of variation in rate of blowing and have developed an equation from which variation in blow-gas composition with blast pressure may be inferred.

(v) *The Depth of Fuel Bed.*—The fundamental incompatability of the need for a shallow fuel-bed during the blow and a deep fuel-bed during the steaming has led to special designs of plant, *e.g.* Kramer and Aarts (J. Gasbeleucht. 1903, **46**, 921). This consists of twin generators operated in parallel during the blow and in series during the run. The Dellwik-Fleischer generator operates with a shallow fuel bed and a low steam rate (*ibid.* 1900, **43**, 354).

In plant of more orthodox design it is customary to have a fuel bed of 6 ft., and variation of this depth is suggested by F. J. Dent (Trans. Inst. Gas. Eng. 1935–36, 222) to compensate for fluctuations in coke size and wetness. No advantage is to be gained by adopting a shallow fuel-bed as standard because costs rise as a result of a lower thermal yield of gas and the gas output is reduced.

The fuel bed functions as if it were a reaction zone between a mass of coke and a mass of clinker which act as heat generators. Reducing the depth increases the loss of sensible heat from the fuel bed. The optimum depth is, therefore, that which avoids excessive loss in sensible heat in the gas without causing undue resistance to gas flow.

(vi) *The Nature of the Fuel.*—The carbonaceous materials that have been used for production of water gas include coke, bituminous coal, semi-coke, crude lignite and lignite briquettes. These vary in their volatile-matter content, caking power, tendency to disintegrate, grading, ash fusibility and inherent reactivity. Generator design has, therefore, been modified to overcome the special difficulties. For example, a fuel containing appreciable volatile matter may be gasified in a generator fitted with a superimposed carbonisation shaft in which the sensible heat of the water gas produced in the generator proper is used to expel the volatile matter in the freshly-fed material.

In this country, where coke is commonly used, it is recognised that desirable characteristics are (*a*) large size and uniform grading (since these influence the resistance of the fire and affect the time of contact), (*b*) a high density which permits the use of a high blasting rate without undue loss of fuel due to blowing over as fliers, and (*c*) an ash which does not clinker readily.

If a material screened above 1¼ in. with 25% above 3 in. is used, the gas output is about 20%

greater than when ½–1 in. material is gasified. Thermal yields would be in the same ratio, due to the greater amount of potential heat lost in the blow gas on account of the greater surface presented to the gases as well as to the lower air rates. These losses can be reduced by adopting a shallower fuel bed. Where the lower cost of smaller fuel compensates for the reduced output and thermal yield, lower grade fuels can be satisfactorily employed.

Moisture in the coke has to be evaporated by the gases leaving the generator and consequently the temperature of these gases is decreased. This fall in temperature may lead to difficulty in igniting the blow gas and may require a change in air-steam ratio to compensate for it.

The reactivity of a fuel bed is a function of its temperature, the surface presented and the inherent reactivity. The temperature is limited by that at which clinkering occurs, whilst the surface presented is determined by the size of the coke, but small coke has overriding disadvantages in other directions. A high inherent reactivity is desirable since, for a given rate of steam decomposition, there is a lower operating temperature and there are smaller losses in sensible heat from the generator. A low reactivity to carbon dioxide and a high reactivity to steam would be desirable in water-gas production, but these two reactivities are usually parallel. Furthermore, initial reactivity is affected by the heat treatment the coke receives in the top of a generator before it descends into the reaction zone. The Fuel Research Board (*l.c.*) have made comparisons of the performance of a water-gas plant when gasifying horizontal-retort coke, vertical-retort coke and semi-coke. The tests were carried out at equal air rates and the water-gas outputs rose with increasing reactivity, viz. 39·7, 42·1 and 45·6 therms per hour. The increase in the output with semi-coke was partially due to residual volatile matter. The water gas from the semi-coke did not show a higher carbon dioxide content, indicating that the effect of any lowering of the fuel-bed temperature is counterbalanced by the greater reactivity to steam. Thermal efficiencies were similar because increased reactivity also involved increased production of carbon monoxide in the blow gas.

Continuous Water-Gas Production.—It has been made clear that when the necessary heat is supplied by blowing with air, the introduction of atmospheric nitrogen necessitates the discarding of the blow gases and the operation of the plant cyclically. It is possible, however, to supply the heat of reaction by the use of oxygen with the steam. *See* H. J. Hodsman and J. W. Cobb (Trans. Inst. Gas Eng. 1919–20, 429) and F. J. Dent (*ibid.* 1936–37, 120).

The continuously operated Winkler generator (Fig. 10) employs a mixture of oxygen and superheated steam, the fuel being small (up to 6 mm.) dried brown coal or semi-coke derived from brown coal. The velocities of the incoming gases are such that the fuel in the generator is kept in a state resembling ebullition, a condition which favours intimate contact and good heat transfer. A generator of 220 sq. ft. cross-section is capable of the enormous output of 42 million cu. ft. of water gas per day. Generators of this type are employed at Oppau and Leuna in Germany for the production of hydrogen for ammonia synthesis and coal hydrogenation. A proportion of the fine fuel is blown over and provision has to be made for freeing the gas from dust by means of direct coolers and electrostatic precipitators. Typical gas compositions have been given (Génie Civil, 1936, **109**, 105):

Composition.	Gasifying mixture.	
	Oxygen and steam.	Oxygen, air and steam.
Composition :	%	%
CO_2	13–20	15·2
CO	47–36	32·9
H_2	39–41	29·7
CH_4	0·6–0·4	1·3
N_2	0·4–0·5	20·9
Raw materials per cubic metre of gas :		
Fuel (kg.)	0·62	0·5
Air (cubic metres) . .	—	0·23
Oxygen at 98% purity	0·27	0·17
Steam (kg.) . . .	0·3	0·2

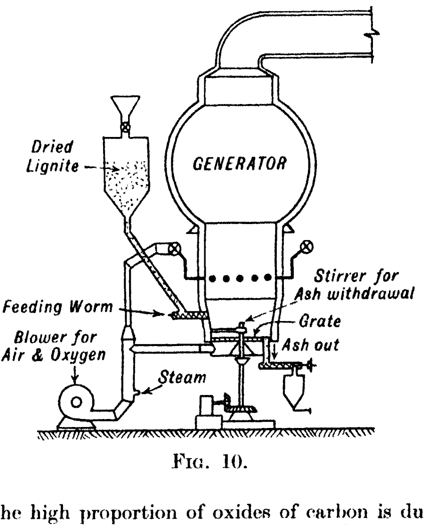


Fig. 10.

The high proportion of oxides of carbon is due to admixture of the combustion products and carbon with the water gas and also to the high percentage of oxygen in the original fuel.

The Lurgi generator (Fig. 11) consists of a water-jacketed vessel of about 3 ft. 9 in. internal diameter which operates with a 10 ft. fuel bed. Operation of the process is restricted to non-caking coals; a large-scale plant at Zittau operates on lignite (*cf.* Arch. Wärmewirt. 1938, **9**, 201). The gasifying medium consists of a mixture of pre-heated oxygen and steam at about 20 atm. and this pressure is maintained in the generator. The fuel is fed into the generator by means of a feed chamber having a bolted cover plate above and a cone feed valve below. With the chamber full of fuel, charging consists of equalising the pressure in the generator and the feed chamber, and then lowering and replacing the cone valve. After blowing off the gas contained in the feed chamber, the cover plate is removed and the feed chamber refilled with more fuel. A similar device below the grate permits the intermittent withdrawal of the ash. Gas production proceeds continuously. High pressure is adopted because it is found that a process is superimposed upon the water-gas production which leads to the production of methane in the upper part of the fuel bed. This production is favoured by pressure, and it would appear that the mechanism depends upon the hydrogenation of the "fixed carbon" of the fuel (Trans. Inst. Gas Eng. 1938–39, 150). F. Danulat (Mitteil. der Metallgesellschaft, 1938, No. 13) has given details of the operation and working results with a plant of this type. An output of 0·62 million cu. ft. of gas of a calorific value of 440 B.Th.U. per cu. ft. was obtained and the oxygen requirements were only 15% of the volume of gas produced. The composition of the gas before and after washing under pressure is :

	Crude.	Purified.
	%	%
CO_2+H_2S	30·6	3·0
CnHm	0·6	0·5
O_2	0·1	0·1
CO	16·5	22·8
H_2	34·0	48·7
CH_4	16·3	22·6
N_2	1·9	2·3

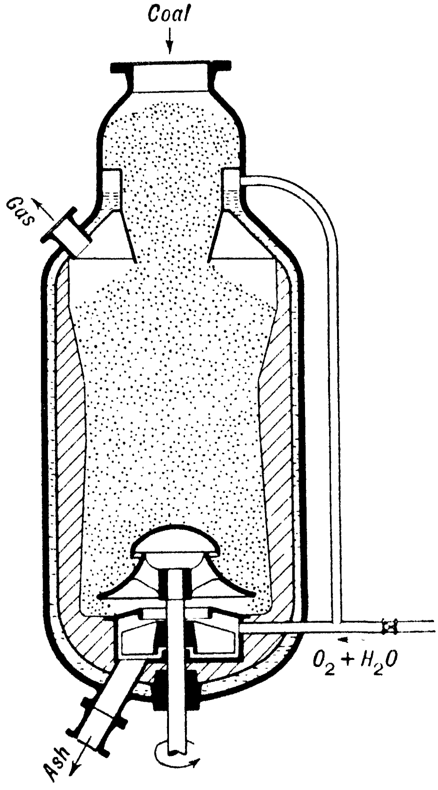


Fig. 11.

The advantages of operation under pressure, besides the raising of the calorific value, are: (i) low velocities through the fuel bed, (ii) simplification of purification and of benzole stripping from the gas, and (iii) ease in transmitting the gas over long distances.

It should be noted that the practice of steaming adopted in the production of town's gas in the continuous vertical-retort is an example of continuous water-gas production. Here the heat of reaction is derived partly from the sensible heat in the coke and partly from heat transferred through the retort walls (*cf.* M. Barash and T. M. Tomlinson, Proc. Intern. Conf. Bituminous Coal, 1931, **1**, 695).

The Pintsch-Hillebrand generator produces water gas continuously without the use of oxygen. The plant consists essentially of a generator mounted upon twin regenerators. Provision is made in the generator for the carbonisation of lignite briquettes in its upper half and for water gas production in the lower half. Each part has a separate off-take. Some of the water gas made is mixed with the products of carbonisation derived from the upper section, and is then preheated in one of the regenerators. The heated gas mixture is then led into the fuel bed, where its sensible heat is expended in the carbonisation of the coal. A portion of the preheated gas is reserved for combustion in the second regenerator, where it is burnt with air, which may be mixed with waste gas to lengthen the flame. By this means the temperature of the regenerator chequer-work reaches about 1,300°. The regenerators are changed over every 15 minutes. Where an external supply of gas is available for heating, the output of gas from the generator may be increased by as much as 65%. A description of the operation of a plant of this type has been given by H. Müller (Chem. Eng. Congress, World Power Conf. 1936, E5), who discusses the advantages of water gas as a source of hydrogen.

Industrial Applications of Water Gas—*Water Gas as a Source of Hydrogen.*—The industrial demand for large quantities of cheap hydrogen has acted as a great stimulus to water-gas production. In the synthetic ammonia industry, for example, the main factor in the cost of production is the cost of the hydrogen (*v.* Ammonia, Vol. I, p. 334).

Methods based on water-gas production which are available for the manufacture of hydrogen on a large scale include the following:

(1) The production of water-gas from coke by the normal (discontinuous) method, followed by

conversion of the carbon monoxide to carbon dioxide and its elimination.

(2) The production of water gas from coke by a continuous method employing oxygen and steam.

(3) The production of water gas from lignite.

(4) The decomposition of gaseous hydrocarbons by means of steam.

(5) Reduction of iron oxide to iron by water gas followed by the passage of superheated steam over the iron to form iron oxide and hydrogen (Lane process).

The production of hydrogen by such processes will be treated under HYDROGEN.

Synthesis Gas.—There is required for the synthesis of methanol or the Fischer synthesis of hydrocarbons, a gas in which the ratio of carbon monoxide to hydrogen is 1:2. The ratio of CO/H_2 in normal blue water-gas is 1:1·25 and the following methods are employed to produce from it a gas of the required composition:

(1) Production of blue water-gas, its purification from sulphur compounds and the conversion of some of the carbon monoxide into hydrogen by catalytic interaction with steam,

$$CO + H_2O = CO_2 + H_2.$$

The unconverted and converted gases are then mixed to obtain the correct proportion of hydrogen to carbon monoxide.

(2) Modification of the water-gas process by introducing debenzolised coke-oven gas along with the steam during the "make" whereby the reaction

$$CH_4 + H_2O \quad CO + 3H_2.$$

augments the hydrogen of the blue water-gas and the hydrogen of the coke-oven gas. For 100 vol. of blue water-gas, 70 vol. of coke-oven gas are needed to give a total of 220 vol. of synthesis gas.

(3) Gasification of semi-coke in an ordinary water-gas generator goes part of the way towards the required ratio, *e.g.* 54% H_2 to 36% CO can be attained. The volatile matter of semi-coke is rich in hydrogen and most of this reappears in the water gas and enriches it in hydrogen.

The coke ovens from which the coke fuel for the water-gas sets is obtained may conveniently provide extra hydrogen.

Another industrial application of water gas is found in nickel metallurgy, where both the carbon monoxide and the hydrogen in the water gas are required in the manufacture of metallic nickel from the ore by the Mond process (*cf.* Anon., Ind. Chem. 1934, **10**, 253). The ore consists essentially of a mixture of the sulphides of nickel and copper and, after extraction of the copper, the matte remaining contains about 56% of nickel. The operation for extracting the nickel consists in reducing it to the metallic state by means of hydrogen, followed by extraction with carbon monoxide as nickel carbonyl, which is then decomposed to give the metal. It is not necessary to separate the hydrogen for the reduction; a supply of water gas is passed directly through the reducer. The reduction process is interesting in that it is accomplished at so low a temperature that the carbon monoxide effects only about 3% of the reduction, some 97% being due to the hydrogen. The reaction with hydrogen, although an endothermic one is, at the temperature employed, from 20 to 40 times as rapid as the exothermic reaction with carbon monoxide. The result of this great activity of the hydrogen in the reduction is to give an end gas which is very rich in carbon monoxide and is thus suitable for the formation of nickel carbonyl.

H. H. and W. A. V.

GATTERMANN REACTION (*v.* Vol. III, 585*d*).

"GAUGING PLASTER" (*v.* Vol. II, 132*d*).

GAULTHERIN (Monotropin), the parent glycoside of methyl salicylate, obtained from *Gaultheria procumbens* L., it contains the disaccharide, primeverose (Bridel, Compt. rend. 1925, **180**, 1864).

GAULTHERIOSIDE. A glycoside obtained from *Gaultheria procumbens* L. It has m.p. 185°, $[\alpha]_D$ −58·07° (anhyd.), and yields on hydrolysis glucose, xylose and EtOH (J. Rabaté and S. Rabaté, Bull. Soc. Chim. biol. 1931, **13**, 604).

GAUSS CELL (*v.* Vol. III, 54*d*).

GEASE (*v.* Vol. IV, 314*b*, 394*d*).

GEDRITE (*v.* Vol. I, 302*d*).

GEGENIONS (*v.* Vol. III, 284*a*).

GEHLENITE (*v.* Vol. II, 146*d*).

GEIJERENE. The hydrocarbon, *geijerene*, $C_{12}H_{18}$, b.p. 85°/17 mm., d_{20}^{20} 0·870, n_D^{20} 1·4888, $[\alpha]_D \pm 0°$, occurs in the essential oil from *Geijera parviflora* (Penfold, J. Proc. Roy. Soc. New South Wales, 1930, **64**, 264; Penfold and Simonsen, *ibid.* 1932, **66**, 332). The hydrocarbon is monocyclic and contains three ethylenic linkages, one of which is present as a methylene group, but no further evidence as to its structure is available. *Hexahydrogeijerene*, b.p. 96°/20 mm., d_{25}^{25} 0·8373, n_D^{25} 1·4577, has been prepared by the catalytic hydrogenation of geijerene.

J. L. S.

GEIN (*v.* IV, 394*d*).

GEISSOSPERMUM VELLOSII, ALKALOIDS OF. From the bark of *Geissospermum Vellosii* (Fam. Apocynaceæ) (syn. Tabernaemontana lævis Vell., Geissospermum læve (Vellozo) Baillon, vulg. Pao Pereiro, Pau Pereira) an amorphous brownish-yellow extract is obtained which since long is used as a febrifuge under the name of "pereirine" in Brazil. For history and botany of pereiro-bark, *see* Raymond-Hamet, Bull. Sci. pharmacol. 1937, **44**, 449.

It was Hesse who first isolated from pereiro-bark the two alkaloids *geissospermine* (I) and *pereirine* (II) (Annalen, 1880, **202**, 141) and a third alkaloid *vellosine* was found by Freund and Favet (Ber. 1893, **26**, 1084; Annalen, 1894, **282**, 247). References to early literature may also be found in the papers by Bertho and co-workers (Ber. 1931, **64** [B], 2278; Annalen, 1934, **509**, 241) who re-examined the plant and gave the following details:

Geissospermine (I), $C_{40}H_{50}O_3N_4 + 1\frac{1}{2}H_2O$, from aqueous MeOH, $[\alpha]_D^{20}$ −101·9° (EtOH) or (I) $+2H_2O$ from ethyl acetate or benzene,

$[\alpha]_D^{20}$ −108·2° (EtOH). Two of the four N-atoms of geissospermine are basic, it yields neutral salts with 1 mol. of a dibasic acid and combines with 2 mol. of methyl iodide. The salts are crystalline; it contains one -OMe group and a labile basic -NMe group. For colour reactions, *see* Raymond-Hamet (*l.c.*).

Pereirine (II), $C_{20}H_{26}ON_2,0{\cdot}5H_2O$, $[\alpha]_D$ +137·5°, amorphous, yellowish coloured powder with intensely bitter taste (whereas (I) is tasteless). (II) is obtained from the mother-liquors of (I) and is readily soluble in EtOH, MeOH, Et_2O, ethyl acetate, benzene, and $CHCl_3$. (II) does not contain -OMe or -NMe groups. The salts, the methyl ether, and the methiodide are also amorphous.

Vellosine (III), $C_{23}H_{28}O_4N_2$, $[\alpha]_D$ +22·8°, m.p. 189°, crystallises from EtOH, it contains two -OMe groups and behaves as a monoacidic tertiary base. The salts are crystalline, and physiologically it resembles brucine.

The constitution of the three Geissospermum alkaloids is unknown, although the work of Bertho and co-workers makes it probable that these alkaloids are indole- or perhaps harmane-derivatives. By treating geissospermine with alcoholic HCl its apparently symmetrical molecule is split into two equal halves :

$$C_{20}H_{26}N_2O_2+\tfrac{1}{2}H_2O,$$

$[\alpha]_D^{20}$ −57·4°, m.p. 115°, amorphous, readily soluble in MeOH, EtOH, acetone, etc., only slightly soluble in benzene, $CHCl_3$ and Et_2O. The salts and the methiodide are also amorphous.

Freise (Pharm.-Ztg. 1936, **81**, 241) has isolated from strychnos spp. curare-like alkaloids among which there is a base very similar to or identical with vellosine.

Schl.

GELATIN.—Gelatin is the first hydrolytic product of collagen. Commercial gelatin is the purest form of glue (*q.v.*) and is made from hide or skin trimmings or bones by similar methods but with greater precautions to ensure purity, especially in the case of the photographic and edible varieties.

MANUFACTURE.—(*a*) *Hide and Skin Gelatins.*—These constitute a large proportion of the supply. The raw material has to be carefully chosen. Hide and calf pieces (trimmings such as ears, cheek-pieces, pates, fleshings, etc.), make the best gelatin. Sheep spetches, hand fleshings and goat and deer pieces are also used but give a darker product. These may come in the green or dry state from the slaughter house or after treatment with a lime suspension from the tannery. The presence of sodium fluoride or silicofluoride in the curing salt does not lead to an abnormal amount of fluorides in the gelatin (Jordan-Lloyd, Collegium, 1933, 698; J. Soc. Leather Trades' Chem. 1934, **18**, 501), but arsenic and bacterial contamination must be absent.

The *first* process is a thorough washing in tumbler or barrel mills to remove salt from "green" stock and cleanse limed stock. It is customary to run the material through a shredding or pulping machine at this stage to obtain greater uniformity in the subsequent treatment.

The *second* process consists in treatment with a lime suspension. This extracts some of the non-gelling constituents, saponifies fatty material and opens up the collagen fibres, causing separation into fine fibrils which, in their turn, are separated further into the long colloidal molecules of gelatin, which are soluble in hot water. This liming operation is carried out by dumping the stock into concrete or wooden vats containing the lime liquors and turning frequently to ensure even distribution. Several complete changes of lime liquor are used and the total amount of lime required varies from 5 to 10% of the weight of the stock, and should be free from iron and manganese. The time taken depends on the kind and condition of the stock and may be 14–60 days. Treatment is complete when the stock is plumped and relatively free from grease. The time may be reduced by the use of "sharpeners" such as caustic soda. The temperature is a very important factor and should not exceed 20°C. otherwise the gelatin yields sensitive emulsions which tend to fog. The whole process should be very carefully controlled to avoid bacterial growth which is liable to be present in old liquors.

The *third* process is a thorough washing in the mills which should not be continued after the wash-water runs clear and shows only a faint colour with phenolphthalein. Prolonged treatment results in the hydrolysis of the gelatin, which reduces the gelling temperature, the melting-point and the viscosity. The water supply should contain not more than 10–15 grains per gallon of calcium and magnesium salts, and be as free as possible from iron, hydrogen sulphide, sodium carbonate, chlorides, ammonia, moulds and bacteria. Salts tend to soften and liquefy the gelatin. Formaldehyde (1 in 100,000) or other antiseptic may be added.

The *fourth* process is careful neutralisation with sulphuric or, better, hydrochloric or sulphurous acids. The acid is added to the wash-water in the mills to get even action. Sulphuric acid gives calcium sulphate which is difficult to wash out. Hydrochloric acid must be free from traces of iron and arsenic. Sulphur dioxide is very detrimental in high quality gelatin. The stock should be rendered neutral to Methyl Orange or Congo Red and must not redden phenolphthalein. Acidity and alkalinity both lead to hydrolysis in the cooking and so it is necessary to bring the stock to a neutral condition with a p_H value of about 5·0 (Goebel, Gelatin, 1934, **2**, 66, 75). It is then well washed with cold water in a revolving cylinder or paddle to remove the salts formed in order to obtain a product with a low ash.

The *fifth* process is the cooking, which is usually carried out in large aluminium or wooden vats provided with water feed-pipes and false perforated bottoms, below which are steam-coils for injecting steam. The stock is covered with hot water and heated. For higher grades of gelatin, temperatures from 55–80°C. are maintained for several hours. Fractionated cooking is usually practised, the liquor being drawn off through a valve in the bottom of the vat, fresh water added and a further extraction made at a slightly higher temperature. The first and second runnings are the best, the third and fourth yielding size. The residue is used as a fertiliser. In France, batteries of closed metal kettles are in general use.

The *sixth* process is clarifying by settling or press filtration. The liquor from the boiling floors is sometimes run into large shallow vats and kept warm so that the grease rises to the surface and insoluble matters separate out. Usually the liquors are passed through coarse filters to remove undissolved organic matter, albumins, mucins, lime soaps and mineral particles. Further filtration is then effected by the use of press filters filled with cellulose. Or the liquors may be clarified by the use of potash alum or the addition of egg albumen solution to the cool mixture, the temperature then being gradually raised until coagulation takes place. After settling for some hours the clear liquor is siphoned off and filtered.

The *seventh* process is concentration. This cannot be effected by simple evaporation because a skin would form and the interior portions would lose their jellying power. The aerobic system consists of rotating cylinders half in and half out of the liquor at 70–80°C. The Yaryan or climbing film type of evaporator (*v.* EVAPORATION, Vol. IV, 409*d*) is in more general use because heating at 70°C. impairs the setting power of the gelatin. The water-absorbing capacity of gelatin depends upon the concentration at which it is set prior to drying. For thin sheet varieties this is usually stopped at 5–6% as shown by a hydrometer, and setting is effected by chilling in shallow metal trays in a refrigerator, or by feeding over a series of slowly moving chilling rollers, cooled internally by brine. The operations of chilling, cutting up, placing on metallic frames and drying are usually carried out by machine so that the gelatin is not touched by hand.

The *eighth* process consists in bleaching with sulphurous acid or hydrogen peroxide, but this is only necessary where low grade raw material has been used.

The *ninth* process, the drying, must be very carefully controlled because slow heating favours hydrolysis, bacterial and mould growth, whilst prolonged heating impairs the gelatinising power. The temperature must not exceed 20°C. or the gelatin may soften or melt. It is thus best to dry *in vacuo* or in a chamber in which the velocity, temperature and relative humidity of the air current are controlled. The speed of the hydrolysis is least if the p_H range is 4·7–6·0 (Stupholme, Food Manuf. 1938, **13**, 46). The water-content should be reduced to 10–15%. If higher a flexible product with poor keeping quality is obtained. If lower the gelatin is brittle and has reduced jellying power. Sheet, cake, leaf, pearl, powdered, flake, kibbled and pressed foam preparations of gelatins (Sheppard and Hudson, Ind. Eng. Chem. 1936, **28**, 422) are on the market.

(*b*) *Bone Gelatin.*—High-grade commercial gelatin is also made from ossein and horn-pith, whilst horns, intestines, bladders, fish-bones, etc., are used for the crude varieties. The ossein is made by slowly pumping 6–8% hydrochloric acid (free from arsenic and iron) in counter-current system through the degreased bones in large wooden vats for 5–10 days to remove the mineral constituents, chiefly calcium phosphate and carbonate. The acid liquor, saturated with the calcium salts, is discharged for recovery of the phosphate for use in fertilizers, bone china and phosphate baking powder. Sulphuric acid is not suitable owing to formation of insoluble calcium sulphate. A solution of sulphurous acid in a closed tank is frequently used because it bleaches and can be recovered. It is necessary to remove by thorough washing all the mineral constituents from the bones and the soluble salts formed. The residual acid is neutralised with lime-water. The ossein is then limed for 6–7 weeks with lime suspensions to plump it and remove the mucins. The effect of liming is discussed by L. Meunier and P. Audry (J. Soc. Leather Trades' Chem. 1935, **19**, 408). It is then treated as with hide gelatins. The yield from ossein is 65–85% of gelatin.

PROPERTIES.—The properties of gelatin are influenced by the collagen from which it was made, by the concentration at which the strong solution set, by even small traces of mineral salts and by drying. Commercial gelatin contains 1·2% ash of which 0·2–0·5% is lime, 8–15% of water; gelatoses and peptones. Bone gelatin contains traces of sulphites and phosphates (Procter, Kolloid-Beih. 1911, **2**, 243). This is no disadvantage either for edible uses or for adhesives, but further purification is necessary for some photographic gelatins and to obtain a pure material for research purposes. Purification can be effected by washing with a mixture of dilute hydrochloric acid and sodium chloride, and dialysing at the isoelectric point (p_H 4·7) until free from chlorides (Smith, J. Amer. Chem. Soc. 1921, **43**, 1350; Jordan-Lloyd and Pleass, Biochem. J. 1927, **21**, 1352), or it can be effected by electro-dialysis, which is stated to effect the separation of a more soluble and a less soluble form (Schryver and Thimann, *ibid.* 1927, **21**, 1284; Knaggs and Schryver, *ibid.* 1924, **18**, 1079) or by electrolysis of a gelatin gel between platinum electrodes (J. Swyngedauw, Compt. rend. Soc. Biol. 1937, **126**, 33, 35; Kolloid-Z. 1938, **83**, 230). Electrolyte-free gelatin acquires the power to flocculate gold sols after ultra-violet radiation.

Gelatin is generally an amorphous, brittle, transparent, colourless, tasteless, inodorous substance. It is neutral to test paper and absolutely permanent in dry air. When moist or in solution, it rapidly putrefies and possesses the characteristic property of becoming acid at the commencement of the change, although ammonia is finally evolved. It has a specific gravity of about 1·3 and no definite melting-point, but begins to soften with decomposition at about 140°C. It is insoluble in cold water, alcohol, chloroform, carbon disulphide, ether or hydrocarbons but dissolves readily on heating with benzyl alcohol (Overhoff, 10th Internat. Congr. Chem. Rome, 1938; J. Soc. Leather Trades' Chem. 1938, **22**, 473). It dissolves in warm water (except if pure, when it is only very slightly soluble even at 100°C.) forming electrically neutral, multipolar zwitterions at the isoelectric point (p_H 4·7). The solution contains a large amount of gelatin A, which is stable above 35°C. and has a specific optical rotation of –313°, and very little gelatin B, which is stable only below 15° and has a specific optical rotation of –141° (Smith, J. Amer. Chem. Soc. 1919, **41**, 135). Salts reduce this mutarotation. A crystalline variety of gelatin also exists (Bradford, Nature, 1923, **111**, 200).

Gelatin dissolves in dilute salt solutions and its solubility greatly increases in strong solutions of nitrates, iodides and sulphocyanides and in strong solutions of urea. A 15% barium chloride solution dissolves sufficient gelatin to make it syrupy and the solution keeps well. Strontium chloride has a similar but less effect. It is readily soluble in $N/1$ sodium salicylate. It is soluble in concentrated acetic acid and in mineral acids, and loses its gelatinising power, but the solution forms a powerful cement for glass, etc. *Dumoulin's liquid glue* consists of a solution of 2 lb. glue or gelatin in 1 quart of water and 7 oz. nitric acid (1·355 sp.gr.). Gelatin is soluble in the cold in alkalis and this solution, as well as the acid solution, is lævorotatory. On the other hand, gelatin reduces the solubility of easily soluble salts and increases the solubility of difficultly soluble salts. More lime is dissolved by gelatin solutions than by water.

Ash-free gelatin contains 49·4% of carbon, 6·8% of hydrogen, 18·0% of nitrogen, 0·7% of sulphur and 25·1% of oxygen (Chittenden, J. Physiol. 1891, **12**, 33). Later analyses confirm the presence of sulphur but it is difficult to obtain it free from ash and peptone. Dakin's technique (Biochem. J. 1918, **12**, 290; J. Biol. Chem. 1920, **44**, 499) for separating individual amino-acids in protein hydrolysates by extraction with butyl alcohol accounted for 91·3% of the amino acids separated or else estimated from van Slyke's data (*ibid.* 1911, **9**, 185). This is equivalent to about 80% of the molecule. Atkin (J. Soc. Leather Trades' Chem. 1933, **17**, 575; 1937, **21**, 513) has amended the percentages of the various amino-acids, thus accounting for 79·27% of the gelatin molecule, 25·5% glycine, 19·4% proline and 14·4% hydroxy-proline are the main constituents. Tryptophane is absent but histidine, tyrosine and cystine are present in small amounts. The part unaccounted for corresponds to mono-amino-acids only and its average residue weight is 123. The whole number of molecules of amino-acids is 360 in a molecular weight of 34,500, which is in harmony with the average dimensions as deduced from X-ray analyses (Astbury and Atkin, Nature, 1933, **132**, 348).

The properties of gelatin solutions are greatly influenced by their p_H value. The solubility and degree of dispersion in solution increases rapidly on either side of p_H 4·7. On the acid side, the curve of combined acid rises regularly with decreasing p_H up to a level region at about p_H 2. The curve of combined alkali rises rapidly with increasing p_H until nearly p_H 7, then gets less steep, but rises again at higher p_H values. Neutral salts cause increased fixation of acid and alkali. On deamination there is a fall in the acid-binding power and in the swelling.

Gelatin is completely precipitated by half-saturation with ammonium, zinc or magnesium sulphates, sodium chloride in the presence of a little acid, trichloroacetic acid and phosphotungstic acid. A saturated solution of picric acid completely precipitates gelatin at 8°C. On the other hand it fails to give the glyoxylic, Millon and sulphur tests (in spite of the presence of sulphur) and produces only a slight xanthoproteic reaction. It is not precipitated by normal lead acetate or ferrocyanic acid. Thus it is not a typical protein and resembles the albumoses.

Gelatin is precipitated by tannin in acid solution, provided that it is not present in excess, forming a compound of variable composition which is not capable of employment as a leather on account of its lack of structure. It is also "tanned" by salts such as alum, chrome alum, basic chromic and iron salts, which diminish the solubility and raise the melting-point of the jellies. Bichromated gelatin, which becomes insoluble and does not absorb water after exposure to light, is used in carbon printing, photolithography, other photo-mechanical processes and in cement making. Gelatin also combines with silver in alkaline solution to form gelatin-silver compounds, which blacken on standing in the light. Gold chloride, platinic sulphate, stannous chloride and mercuric chloride also precipitate gelatin. Moist gelatin combines with 15·4% of chlorine (reckoned on the air-dry basis) yielding an extremely stable insoluble compound. Cross, Bevan and Briggs (J. Soc. Chem. Ind. 1908, **27**, 263) adapted this reaction to the estimation of gelatin in tub-sized papers. Traces of formaldehyde increase the tenacity and flexibility of gelatin, but even small quantities render it insoluble, producing a hard, elastic, imperishable product which is almost unaffected by water. Gelatin is used as a surgical dressing and as a disintegrator for medicinal tablets.

The hydrolysis of gelatin is a very important matter because its properties are determined by the extent to which this takes place. Proteoses (gelatoses, albumoses), peptones, simple polypeptides (kyrines) and amino-acids are formed and may all be present together. Alkalis have a more powerful action than acids, cold lime-water dissolves gelatin in a day or two and it is not precipitated on neutralisation. On prolonged heating with concentrated hydrochloric or 25% sulphuric acid, gelatin is completely converted into amino-acids. Enzyme hydrolysis is much affected by conditions of temperature, reaction, dilution, etc. Partial hydrolysis with pepsin in acid solution and trypsin in alkaline solution gives well-defined peptones. The latter on further hydrolysis yield a tri-peptide (kyrine) and then arginine, lysine and glutamic acid.

The following are useful tests for determining the extent of hydrolysis and the quality of commercial gelatins: (1) Gelatin is regarded as being insoluble in half-saturated solutions of the sulphates of ammonium, zinc and magnesium; the proteoses as insoluble in saturated solutions whilst peptones and amino-acids are soluble in all concentrations of these salts. (2) The fact that a mixture of saturated picric acid solution with 4 parts alcohol precipitates other proteins, but not gelatin, has been applied to a method of estimating gelatin in presence of other proteins (Berrar, Biochem. Z. 1912, **47**, 189). (3) The amount precipitated by alcohol is often taken as an index of its quality. 25 c.c. of 10% gelatin solution is treated with 75 c.c. of absolute alcohol. The coagulum is washed with dilute alcohol, cold water, dried and weighed. A good gelatin may give 98% whilst glues may give no more than 60%. The effects of sodium and potassium chlorides in increasing this are additive, but the following salt pairs are antagonistic: $NaCl+CaCl_2$; $NaCl+MgCl_2$; $CaCl_2+MgCl_2$. (4) H. Stadlinger (Chem.-Ztg. 1936, **60**, 305) measures the degree of hydrolysis by $100\ N_2/2N_1$, where N_1 is the nitrogen content of 25 c.c. of a 2% solution of the gelatin or glue in a sodium acetate–acetic acid buffer of p_H 4·7 and N_2 is the nitrogen content of the portion precipitated from 50 c.c. of the gelatin or glue solution by a mixture of magnesium sulphate and sulphuric acid. (5) The most accurate control of the amount of degraded protein present is probably obtained by bringing the gelatin solution to p_H 8·3 (the faintest pink to phenolphthalein) and then adding an excess of neutral formaldehyde. The solution is then titrated with $N/10$ $NaOH$, and for a given volume of gelatin solution the ratio "c.c. $N/10$ $NaOH$/mg. total nitrogen by Kjeldahl" is a minimum when the gelatin is in its purest form. As the long polypeptide chains are broken by degradation, the formaldehyde titration increases (W. R. Atkin and F. C. Thompson, "Procter's Leather Chemists' Pocket Book," London, 1937).

The chief characteristic of gelatin is its power of forming heat-reversible gels. When placed in water below 20°C., the better varieties do not dissolve but swell up by imbibing 5–10 times their weight of water. The presence of acids, alkalies or salts greatly influences the amount of this swelling. At the isoelectric point, the water is present partly as loosely bound water removable by pressure, freezing or evaporation and partly as firmly bound water removable only under conditions which damage the gelatin. This imbibition is accompanied by an evolution of heat and a contraction in total volume. The transparent jelly melts at 24–45°C. according to quality, and the solution so obtained sets again to a jelly on cooling to 10°C. if the concentration is above 1% or 0·5% if the jelly is highly purified. The best gelatins set rapidly. Prolonged or repeated heating reduces and finally destroys this property on which the value of gelatin principally depends, so gelatin jellies should always be prepared by first swelling the gelatin, then pouring off the remaining water, adding further water as required, melting by warming to a temperature not above 50°C. and slowly cooling. A solution heated to above 70°C. coagulates and never returns to its original state. In the case of highly purified gelatin, the 10% gels are clear and stable; from 10 to 2% the gels are turbid, with a turbidity increasing with diminishing concentration, but are stable at least up to 2 days. Below 2% the gelatin shrinks to a white clot which falls to the bottom of the vessel leaving clear fluid above (Jordan-Lloyd, Biochem. J. 1922, **16**, 530). Small quantities of electrolytes prevent this synæresis.

Neutral salts exert a lyotrope effect and may favour swelling (iodides, nitrates) or hinder it (sulphates), but in all cases they diminish the rigidity of the jelly framework. The peptising effects of salts vary. In the case of a 5% solution of gelatin containing 33% of the following salts (or saturated in the case of ammonium chloride and potassium nitrate), with potassium chloride, rapid setting of the solution takes place on cooling; with ammonium chloride or magnesium chloride, delayed setting; with zinc chloride, potassium nitrate, ammonium nitrate or potassium thiocyanate, no setting. If the salts are removed by dialysis, the sols set to gels. If the salts are restored to the system it again becomes liquid (Briggs and Hieber, J. Physical Chem. 1920, **24**, 74).

Minimum swelling is obtained at the isoelectric point, but it is much greater in dilute acid and alkaline solutions. In the former it is influenced by the nature of the acid as well as the $H^\bullet$ concentration. With increase of concentration at 18°C., it rises to a maximum at p_H 2·7 and then falls. Increase of the temperature increases the swelling, but the positions of the maxima and minima on the p_H scale are affected. The alkaline curve has a broadly defined step at p_H 7–8 and a maximum at p_H 10. Neutral salts depress acid and alkaline swelling at low concentrations, the effect being a function of the valencies of the anions and cations. Ionisable gelatin salts are formed and the presence of a colloidal gelatin ion produces a membrane equilibrium at the gel–water interface, resulting in an excess of diffusible ions in the gel. Thus there is excess of osmotic pressure in the gel causing swelling which is balanced by its coherence. From experimental values for the volume of the jelly and the external acid concentration, the concentrations of internal acid and ionised gelatin salt can be calculated. Neutral salts repress acid and alkaline swelling (Procter, Kolloid-Beih. 1911, **2**, 243; J.C.S. 1914, **105**, 313; Procter and Wilson, *ibid.* 1916, **109**, 307; Jordan-Lloyd and Pleass, Biochem. J. 1927, **21**, 1352).

The structure of gelatin jellies has been much discussed. Zsigmondy showed that 0·1–0·2% solutions are heterogeneous after 2 days' standing and thus possess a cellular, sponge-like structure, but a solution prepared at the boiling-point shows a homogeneous light-cone in the Siedentopf-Zsigmondy ultramicroscope. Gelatin sols give a very diffuse X-ray diagram (Gerngross and Katz, Kolloid-Z. 1926, **39**, 181; Katz and Gerngross, *ibid.* 1926, **40**, 332; Gerngross, Herrmann and Lindemann, *ibid.* 1932, **60**, 276) and are thus solutions of large molecules. Gelatin gels show an X-ray diagram of the "powder" type very similar to that given by collagen fibres. Setting to a jelly thus occurs when the scattered molecules come together to form a similar structure. The mechanical and optical properties belong to the solid framework whilst crystalloids (sodium chloride, copper sulphate) diffusing into the gel travel in the interstitial fluid phase. The rate of diffusion is very little less than that through water but is reduced by increasing the viscosity of the jelly by means of glycerin. It is the same in undeformed and permanently mechanically deformed gels. Liesegang rings are formed when potassium chromate diffuses into a gelatin gel containing silver nitrate. Gelatin jellies are liquefied by some types of bacteria with decomposition into peptones.

The viscosity of gelatin solutions is very high, but depends upon their previous treatment and history, and is very variable with slight variations in time, concentration and p_H. The viscosity of solutions greater than 1% increases at a greater rate than the concentration and is dependent on the rate of shear. The viscosity of a solution made by heating gelatin in water, when it dissolves entirely as the A form, is constant at the isoelectric point but diminishes with time at all other reactions. On standing below 35° gelatin B develops and the viscosity rises especially at the isoelectric point. The increase of viscosity with time is probably due to the formation of a fine molecular structure—a system of catenary threads (Bogue, J. Amer. Chem. Soc. 1922, **44**, 1313, 1343). With 0·5% gelatin, both viscosity and elasticity show minima at the isoelectric point. Viscosity shows maxima at p_H 2·7 and 7·2; elasticity at 3·5 and 5·5. Added salts reduce viscosity, the effect depending on the valency of the oppositely charged ion and on its lyotropic nature.

Edible gelatin is largely used for culinary purposes as a vehicle for other materials. Gelatin prepared from bones was largely used by the soldiers and poor of France during the first Revolution, but the idea that its high proportion of nitrogen renders its valuable as a flesh-former is erroneous because indispensable amino-acids are entirely missing. It is, however, of limited value as a heat-producer instead of fat and carbohydrates. Taken as a supplementary protein to vegetable proteins, it is valuable on account of its high content of lysine. It is readily attacked by pepsin with hydrolysis of its peptide linkages, the optimum p_H of digestion being about 1·2. Crystalline trypsin hydrolyses gelatin more quickly than chymotrypsin. Gelatin is able to function as a protective colloid in preventing coagulation of milk during digestion and, also, in improving the texture and keeping qualities of ice cream. It is added to fruit preserves, jams, meat extracts, cream, etc., to give a fictitious body. It does not possess antigenic properties due to its deficiency in tyrosine, tryptophane and cystine. It is largely used in bacteriology. Pharmaceutical uses include surgical dressings such as Court plaster, which is a mixture of gelatin, alcohol and glycerin; capsules for medicine; and coating pills. It is valuable for taking casts and impressions for electrotypy, etc., in dyeing, for making inking rollers for printing, and as a size for paper-making and painting. It is used in the carbon process of photographic printing, which depends upon the property of potassium dichromate of rendering gelatin insoluble when exposed to the action of light. This property is also used in making an insoluble glue or a waterproofing material, by adding potassium dichromate to gelatin or glue just before use.

A large amount of the highest quality gelatin is used for photographic films, plates and developing papers. In judging its value for this purpose, Sheppard (" Gelatin in Photography," p. 117, London, 1923) gives the following requirements: (1) It should give a clear and nearly neutral solution. (2) The percentage of moisture should not be greater than 20% and lower for " soft " gelatins. (3) The ash should not exceed 2%. Bases and heavy metals should not be present in more than mere traces, as they are harmful to photographic emulsions. Sulphates and chlorides should be low. (4) Chondrin is objectionable as it causes gelling in hot solution, especially when alum is present. (5) Formaldehyde should be absent. A rose colour should not be given on heating 10 g. with 20 c.c. water to about 105°C., distilling with steam and adding to the distillate a few drops of dilute phenol solution followed by concentrated sulphuric acid. (6) Sulphites should be absent. (7) The darkening or precipitation on mixing a 1–2% solution with an equal volume of 10% silver nitrate (containing ammonia sufficient to redissolve the precipitate) should be according to the user's specification.

In practice it is usual for the consumer to find by experience the most suitable gelatin for his purpose and check future deliveries in respect of those properties which are relevant. The British Standard No. 757—1937, Methods for Testing Gelatines (British Standards Institution) may be used. The physical tests include: (1) Jelly strength, (2) Viscosity, (3) Melting point, (4) Foam, (5) Water absorption, (6) Solubility of partially swollen sheet, (7) Keeping quality, (8) Colour of jelly and of solution, and (9) Clarity, but the first three are usually taken as an index of the grade. The *adhesive strength* is sometimes inferred from the jelly strength, viscosity, melting point and tensile strength, the last is influenced by electrolytes, the effects being in direct relationship to the lytropic series; it is reduced by salts with a strongly hydrated anion (Pavlov and Engelstein, Kolloid. Shurn. 1936, **2**, 821; Merckel, Kolloid-Z. 1937, **78**, 41, 339). The adhesive strength is reduced by prolonged heating and increased by sodium fluoride, sugars and substances containing **OH** groups. The *rate of solution of partially swollen gelatin* in a restricted amount of water varies and the following test may be used to discriminate between different samples: 20 g. of the sample, crushed to pass a ⅛ in. mesh sieve, is added all at once to 20 c.c. of water at 27°C. in a small basin. It is stirred continuously until all the water has been absorbed and left for 24 hours at 18–20°C. in a closed vessel containing water to give a relative humidity of 95–100%. It is then added to 500 c.c. water at 60°C. in a beaker, stirred gently for 4 minutes at 60°C., and poured through a 200 mesh sieve. The residue is rinsed with cold water, transferred to a weighed stainless steel dish and dried at 105°C. to constant weight. This is divided by 0·85 to bring to a gelatin basis and multiplied by 5. The result is expressed as per cent. insoluble residue of sheet gelatin swollen at 1:1. The *colour* is expressed in Lovibond units for a 6·66% w/w gel in a 2 in. Lovibond cell, after keeping for

2 hours at 15°C. If the colour of the sol is desired the temperature should be adjusted to 40°C. To 7·5 g. of the powdered sample, 105 c.c. of cold distilled water is added and it is allowed to soak for 3 hours at 15–22°C. It is heated on a water-bath (not above 70°C.) for 15 minutes at not above 60°C. and gently stirred. The colour is determined with a standard B.D.H. Lovibond Tintometer using artificial light. The *clarity* is determined by measuring photoelectrically the light transmitted through a 6·66% w/w gelatin solution contained in a 2 in. Lovibond silvered cell, and is expressed as a percentage of the light transmitted through distilled water under the same conditions. The standard apparatus consists essentially of a Weston photronic photoelectric cell connected to a microammeter of not greater than 100 ohms resistance. The sensitive face of this cell is illuminated by a parallel beam of light from a source, the intensity of which is adjusted so that when the Lovibond cell containing distilled water is placed in the path of the beam a reading of 100 m.a. is obtained. When the Lovibond cell is substituted which contains the gelatin solution (prepared as previously described), the current recorded measures directly the clarity of the sample.

The chemical analyses are :

(1) *Moisture Content.*—Air-dry gelatin contains 8–15% moisture. Over-dry gelatin is brittle and probably somewhat denatured, whilst it is readily attacked by moulds and putrefactive bacteria when insufficiently dried. The percentage loss in weight when a thin evenly distributed film of the gelatin is dried at 105°C. to constant weight is determined. 1 g., broken up to pass through a B.S. 10 mesh test sieve, is weighed into a tared, flat stainless steel dish (70 mm. diameter, 15 mm. high and weight 20–30 g.). 10 c.c. distilled water is added. After allowing the gelatin to soak, the dish is placed on a water-bath to dissolve the gelatin and then evaporate most of the water. The dish is transferred to an oven at 105°C. ± 2°, left there for 2 hours with the thermometer bulb ½ in. above the centre of the dish and the 105°C. mark about 2 in. above the outside top of the oven. The heating is continued for ½-hour periods until the weight is constant to 1 mg. In crushing and sampling the rapid alteration in moisture-content of finely divided gelatin with the humidity of the air must be avoided.

(2) *Reaction* (p_H).—This is a very important criterion of quality and should be about 4·9 for pure varieties. 1 g. of the powdered sample is dissolved as previously described in a small quantity of warm, recently boiled, distilled water in a stoppered flask of chemically resistant glass and the volume made up to 100 c.c. with recently boiled and cooled distilled water. After shaking and allowing to cool to 18–20°C., the p_H value is determined by the glass electrode. The amount of free acid can be determined by titrating with phenolphthalein.

(3) *Grease.*—The grease content should be negligible. 10 g. of the powdered sample is soaked in 15 c.c. of cold distilled water in a porcelain basin until all is absorbed and heated on the water-bath until dissolution is completed. 40 c.c. of *N*-alcoholic potash is added, the solution evaporated on a water-bath and the residue dried at 105°C. This is then dissolved in 100 c.c. of 10% hydrochloric acid, kept on the steam-bath for ½ hour and transferred to a separating funnel making the volume up to 100 c.c. When cool 50 c.c. of ethyl ether is added. After mixing thoroughly but not vigorously enough to form an emulsion, it is allowed to separate and the ethereal solution run into another separating funnel. This procedure is repeated twice with further 50 c.c. portions of ethyl ether. The ethereal solution is washed with cold distilled water until free from acid, transferred to a tared flask and the ether distilled off on a water bath. 3 c.c. of pure acetone is then added and evaporated off for 2 minutes on the steam-bath in a gentle current of air from a bellows. The flask and dry residue are cooled in a desiccator and weighed.

(4) *Ash.*—The ash content is one good index of the degree of purity. Care has to be taken to ash at as low a temperature as possible as many gelatins contain chlorides which are easily volatilised. It is advisable to check the possibility of overheating by carrying out chloride tests on the ash and on the original sample. This is done by adding 10 c.c. of cold water to 5 g. of the powdered sample in a nickel basin. After soaking for 1 hour, heating on a water-bath and adding 5 g. of pure lime, it is dried on a steam-bath. The organic matter is completely ashed and the salt determined in the water-extract after neutralising with acetic acid.

(5) *Sulphur Dioxide.*—For arbitration purposes in the food industry the method of G. Monier-Williams (Reports on Public Health and Medical Subjects No. 43) is generally used. This consists in distilling 32 g. of the powdered gelatin with 500 c.c. of water and 20 c.c. of concentrated hydrochloric acid in a current of CO_2. The SO_2 is absorbed in 20 c.c. of 3% hydrogen peroxide neutralised to Bromophenol Blue, and titrated with *N*/10 **NaOH** and Bromophenol Blue (*v.* FOOD PRESERVATIVES, this Vol. p. 305*b*).

(6) *Arsenic.*—This is liberated and estimated as parts of arsenious oxide per million of gelatin sample by means of the Gutzeit test in which the solution is reduced with zinc and the arsenic determined by comparing the stain on a mercuric chloride filter paper with standard stains.

(7) *Heavy Metals.*—Lead, copper and zinc should be absent (*v.* FOOD PRESERVATION, METALLIC CONTAMINATION, this Vol. p. 292*b*).

(8) *Fluorine.*—The amount of fluorides found in gelatin from fluoride-treated hides is 0·13–0·16% as compared with 0·02–0·10% from normal hides (Jordan-Lloyd, Collegium, 1933, 698). It is determined to within 10% in the distillate after a single distillation with sulphuric acid by the peroxidised titanium method (Stuart, Dahle and Frey, J. Assoc. Off. Agric. Chem. 1933, **16**, 612; J. Amer. Leather Chem. Assoc. 1937, **32**, 205) (*v.* FOOD PRESERVATIVES, this Vol. p. 298*c*).

Chondrin (*q.v.*) differs but little in appearance from gelatin. It is obtained from cartilaginous tissue and has a much lower gelatinising power than gelatin in which it is almost invariably present. When the proportion is high, the gelatin is of considerably less value, especially for the preparation of photographic emulsions, which require a maximum of tenacity. Chondrin is precipitated from aqueous solution by acetic acid and is not soluble in excess. Lead acetate, alum, and the sulphates of iron, aluminium and copper also precipitate chondrin. A rough test for detecting the presence of chondrin in photographic gelatin consists in adding a concentrated solution of chrome alum to a 10% solution of the gelatin in hot water. If an injurious amount of chondrin be present the gelatin will set whilst hot. Most photographic gelatins, however, contain but little chondrin.

Isinglass.—This valuable product usually contains from 86 to 93% of gelatin. It is obtained by drying the swimming bladders of various fish, of which the sturgeon of the Volga yields the best quality, but Brazilian (sometimes known as Cayenne), Penang, Indian and Hudson's Bay varieties are also on the market. It arrives in this country either as the unopened bladders, known as lump, pipe or purse isinglass, or as the cut and opened bladders, known as leaf and honeycomb isinglass. Long or short staple, book and ribbon isinglass are respectively twisted, folded in packages and rolled out. The bladders of cod, hake and other fish are also employed.

In preparing Russian isinglass the bladders are first cleansed from blood in hot water, cut open, washed and exposed to the air with the delicate silvery inner membrane turned upwards. This membrane is stripped off, kneaded in damp cloths and dried. Before solution in water the crude isinglass is moistened, cut into strips, rolled out into ribbons and dried. When dry they are shredded by suitable machines.

Although free from chondrin, isinglass is not available for photographic purposes on account of its great solubility and inferior tenacity. For clarifying wines, ciders and beers it is, however, much superior to gelatin, probably due to its fine, net-like structure. Coarse Brazilian isinglass is usually employed and is " cut " or dissolved in sulphurous or other acid before use. It is also used for jellies and in the preparation of plasters.

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D. B.

GELATINE DYNAMITES (*v.* Vol. IV, 241*c*).

" GELIGNITE " (*v.* Vol. IV, 242*a*).

GELOSE, *d*-galactan, $(C_6H_{10}O_5)_{57}$. The characteristic polysaccharide of agar-agar (*q.v.*). It is hydrolysed by acids to galactose.

GELSEMIUM, ALKALOIDS OF. *Gelsemine* (I), $C_{20}H_{22}O_2N_2$, a crystalline alkaloid, occurring in the rhizome and roots of American wild jasmine, *Gelsemiun sempervirens* Ait. (Fam. Loganiaceæ), along with *sempervirine* (II), *gelsemicine* (III) and three rather ill-defined bases gelseminine, gelsemidine and gelsemoidine.

Extraction (Chou, A. 1931, 871, 1172 or Chem. Zentr. 1931, II, 2342, 2891).—Roots of American *G. sempervirens* are percolated with cold EtOH, the percolate concentrated in vacuum at low temperature, the syrupy residue being dissolved in dilute HCl and filtered from tarry material. After standing for 2 weeks, a first crop of crystalline hydrochloride has separated (fraction I). This crop is then treated with hot H_2O which leaves behind *gelsemic acid* (needles from $CHCl_3$, m.p. 205°, with blue fluorescence in alkaline solution, identical with *scopoletin*). The aqueous solution is basified and yields *sempervine* (identical with *sempervirine, see later*). The mother-liquor from the first crystal-fraction (*see above*) is also basified and extracted with $CHCl_3$. The $CHCl_3$-residue after several recrystallisations yields pure *gelsemine* (I). The alkaline mother-liquor from this fraction is neutralised with HBr in order to free it from the last traces of (I) (as insoluble hydrobromide) and the remaining solution is evaporated, the residue dissolved in H_2O again, basified and treated with $CHCl_3$ when *gelsemicine* (III) is obtained. The mother-liquors of (III) yield an amorphous alkaloid with amorphous salts, which may be gelseminine. For extraction of *gelseminine* and *gelsemoidine, see* Sayre, Midl. Drugg. Rev. 1911, **45**, 439. or Chem. Zentr. 1911, II, 1650. The same author (J. Amer. Pharm. Assoc. 1915, **4,** 60) has also extracted a base *sempervirine* which probably is identical with Chou's sempervine (*cf. also* Hasenfratz, Bull. Soc. chim. 1933, [iv], **53**, 1084).

Gelsemine (I) was first isolated from the roots of *G. sempervirens* by Moore (J.C.S. 1910, **97**, 2223; 1911, **99**, 1231) where earlier literature can be found. The root was deleted from the B.P. in 1932, the alkaloid from the U.S.P. in 1926, so that there is no preparation of gelsemium in either Pharmacopœia.

Gelsemine (I), $[\alpha]_D^{24}$ $+10°$ in $CHCl_3$ (Chou) or $+15{\cdot}9°$ (same solvent, Moore) crystallises from acetone in prisms, m.p. 178°, which lose 1 mol. acetone at 120°. (I) is readily soluble in EtOH, Et_2O, benzene, $CHCl_3$ and slightly so in H_2O. The Hydrobromide, chloride and nitrate are crystalline. The methiodide regenerates (I) when heated with 20% aqueous KOH-solution. When boiled with concentrated HCl, (I) takes up the elements of water, yielding apo*gelsemine*, isoapo*gelsemine* and *chloro*isoapo*gelsemine*. (I) contains a hydroxyl-group and forms with acetic anhydride a basic *acetylgelsemine* (m.p. 60–70° from MeOH) or 106° (dry)) (Moore). The colourless solution of (I) in concentrated H_2SO_4 is changed to red, then violet and finally green by addition of a crystal of $K_2Cr_2O_7$.

Sempervirine (II), $C_{19}H_{16}N_2$, optically inactive, was observed by Moore, Stevenson and Sayre, and Chou, but a formula was first assigned to it by Hasenfratz (*l.c.* and Compt. rend. 1933, **196**, 1530). From $CHCl_3$ it forms blood-red prismatic needles, m.p. 223°, from EtOH red ortho-rhombic crystals, m.p. 254°; it is also readily soluble in pyridine, less so in acetone, and insoluble in Et_2O, benzene and light petroleum; in dilute solution in EtOH it shows an intense violet-blue fluorescence. The base is not very stable towards heating. The salts are crystalline and mostly coloured, the nitrate is typical, insoluble in H_2O. (II) dissolves in H_2SO_4 with a bluish-violet fluorescence.

Gelsemicine (III), $C_{20}H_{25}O_4N_2$, $[\alpha]_D^{24}$ -140° (in EtOH), crystallises from acetone in broad orthorhombic prisms, m.p. 171°, readily soluble in EtOH, $CHCl_3$, acetone, less so in Et_2O and benzene, insoluble in H_2O. The hydrochloride and chloroplatinate are crystalline. (III) dissolves in H_2SO_4 to a colourless solution which slowly turns purple.

Recently Chou and his collaborators have investigated *Gelsemium elegans* Gardn. Benth., called Ta-Cha-Yeh and Kou-Wen in China. Although the two plants are said to be identical, the alkaloidal content showed some marked differences. A series of five new alkaloids were isolated besides (I), which occurs in both plants (A. 1932, 101; Chem. Zentr. 1936, II, 1022; J. Amer. Chem. Soc. 1938, **60**, 1723).

Alkaloids of Kou-Wen:

(1) *Koumine*, $C_{20}H_{22}ON_2$, $[\alpha]_D^{23}$ -265° (in EtOH) rhombic prisms from acetone, m.p. 170°, readily soluble in Et_2O and sparingly so in light petroleum. The base cannot be acetylated, the salts are crystalline.

(2) *Kouminine*, amorphous, m.p. about 115°, readily soluble in organic solvents, less so in H_2O; the hydrochloride forms colourless prisms and is optically inactive.

(3) *Kouminicine*, amorphous, apparently not yet obtained pure.

(4) *Kouminidine*, $C_{19}H_{25}O_4N_2$, m.p. 299°, prisms from acetone, slightly soluble in H_2O, the hydrochloride and hydrobromide are crystalline and water-soluble.

Alkaloids of Ta-Cha-Yeh.—Koumine, koumininine and

(5) *Kounidine*, $C_{21}H_{24}N_2O_5$, crystallises from 90% EtOH in rhombs, m.p. 315°, only slightly soluble in most organic solvents, readily soluble in H_2O to an optically inactive, alkaline solution. The hydrochloride is crystalline.

Identification, estimation and standardisation of gelsemium alkaloids. *Cf.* Neugebauer, Pharm.-Ztg. 1933, **78**, 1077; Apoth.-Ztg. 1930, **45**, 80; Pittenger, Amer. Chem. Abstr. 1924, **18**, 1178; Sayre, Amer. J. Pharm. 1912, **84**, 193, etc.

Constitution.—There is nothing known about the constitution of any of the gelsemium alkaloids.

Physiological Action.—Gelsemine is physiologically inactive to mammals (lethal dose 180 mg. per kg. for rats intravenously), but produces strychnine-like effects in frogs. The characteristic physiological action of gelsemium roots is due to gelsemicine (lethal dose 0·08 mg. per kg. for rabbits intravenously), to sempervirine (6 mg. per kg. for rabbits) and to Chou's amorphous base (*see above*; 0·7 mg. per kg. for rabbits). For further details, *see* Henry, "Plant Alkaloids," 3rd ed., p. 615.

Sehl.

" *GELVA* " (*v.* Vol. I, 90*c*, 94*d*).

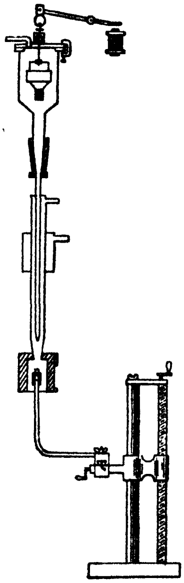
GEMS, ARTIFICIAL. Almost all the mineral species that find an application in jewellery have been prepared synthetically in the laboratory. These artificial products possess the same chemical composition and physical characters as the natural stones, from which they differ essentially only in their mode of origin. It is therefore necessary to distinguish between artificial (*i.e.* artificially produced) gems and imitation and counterfeit gems: the latter will be treated separately in the article GEMS, IMITATION AND COUNTERFEIT.

In nature, these extremely hard and intractable minerals have presumably been formed under conditions of high temperature and pressure during long periods of time. It was therefore not to be expected that crystals of any appreciable size could be produced in the laboratory. The high intrinsic value of the products has, however, offered an incentive to repeated experiments, especially by French chemists; and the production of corundum of gem-quality and of various colours has now been effected with a high degree of commercial success and in a most unexpected manner. Corundum and spinel, and more recently emerald in very limited quantity, are the only gem-stones that have, up to the present, been produced artificially of a size and quality suitable for jewellery.

Several claims have been made of the artificial production of diamond (*q.v.*). The crystals obtained were, however, so small that they could not be submitted to really decisive tests, and their identity is doubtful. The test of hardness was mainly relied upon; but various carbides are capable of scratching corundum, which is the next hardest mineral to diamond.

Corundum was produced artificially first by M. A. Gaudin in 1837, and Frémy and Feil in 1877 succeeded in producing crystals of fair size and of a fine ruby-red colour (E. Frémy, " Synthèse du Rubis," 1891; *v.* CORUNDUM). The largest of these crystals weighed ⅓ carat (0·07 g.) and a few were faceted and mounted as gems, but owing to the extreme thinness of the small platy crystals, they were of no commercial value. About the year 1885 rubies of some size appeared mysteriously on the market, it is said from Geneva: whilst some of these were optically isotropic and softer then true ruby, being of the nature of alumina glass, others were crystalline and identical with natural ruby in their characters. These were known as " reconstructed rubies," and had probably been produced by fusing together small natural stones.

In 1902 A. Verneuil (Production artificielle du rubis par fusion, Compt. rend. 1902, **135**, 791; Ann. Chim. Phys. 1904, [viii], **3**, 20), who had previously assisted Frémy in his experiments, described a new and eminently successful method for the artificial production of rubies of the finest gem-quality. His apparatus consists of an oxy-hydrogen blowpipe placed vertically, the inner oxygen tube of which is enlarged at its upper end to contain a fine sieve holding the alumina powder used in the process. The periodic tapping on the sieve of a small hammer, actuated by an electro-magnet or a rotating cam, causes a small continuous feed of the alumina powder to fall down the oxygen tube. Beneath the nozzle of the blowpipe is a fire-clay support terminating in a small rod of fused alumina, the position of which can be adjusted by screw motions. The blowpipe nozzle and the support are enclosed in a box in order to avoid sudden changes in temperature. Hydrogen was used in the early experiments, but in the commercial process coal-gas is used. The flame, with a temperature of 1800–2000°, must be a reducing one with an excess of hydrogen or carbon. The fine particles of alumina ejected through the nozzle of the blowpipe fall on the alumina support, and, fusing together, build up by accretion a pear-shaped mass, which continues to grow both in height and diameter as the support is gradually lowered.



Verneuil's blowpipe for the artificial production of ruby.

These pear-shaped masses (" boules ") of manufactured ruby (" rubis scientifique," " rubis synthétique ") grow at the rate of about 12 carats per hour, and they may attain a weight of 250 carats (50 g.). One operator can attend to a whole battery of machines. The process is now worked on a commercial scale in France, Germany, Switzerland and Italy; and the output may amount to as much as a ton a day. The price of the uncut material is one or two pence per carat.

The curious feature of these masses of fused alumina is that each one of them is a single individual crystal, and not, as might have been expected, an aggregate of crystals or simply an alumina glass. Although the sides of the drop are usually smooth with a glassy aspect, the rounded end (the last-formed and upper portion in the apparatus) is roughened with a fine crystalline reticulation. Occasionally the drops show a rough hexagonal outline corresponding to the form of a crystal of corundum. The optic axis usually coincides with the axis of the pear-shaped mass, and a section cut perpendicular to this exhibits in the polariscope a typical uniaxial interference-figure. The sp.gr. (3·98–4·0), hardness, dichroism, refractive indices, etc., of this artificial corundum are the same as for the natural mineral. The material further possesses the same transparency, clearness and rich colours as natural crystals of the best gem-quality. The only means of distinguishing between the two is afforded by certain minute irregularities of internal structure. With a hand-lens or under the microscope, the artificial corundum often, though not invariably, shows minute rounded cavities and curved streaks; whilst in the natural stones the cavities are angular and the streaks are straight.

When the material supplied to the Verneuil blowpipe consists of pure alumina powder (prepared by precipitation with ammonia from pure ammonium alum), the crystallised product is perfectly colourless and clear (" white sapphire "). In the early experiments, powdered natural ruby was used as the material. The best ruby-tint is given by the addition of 2½% of chromic oxide (homogeneously mixed with the alumina by precipitating the two together from a mixed solution of ammonium alum and chromium alum). Smaller proportions of chromic oxide produce a lighter shade of red or pink, and such artificial gems have been erroneously called " scientific topaz." The addition of nickel oxide produces a rich yellow colour. Cobalt oxide will not produce a blue colour with alumina alone, but a fine blue is obtained when some magnesia is present (L. Paris, Compt. rend. 1908, **147**, 933; A. Verneuil, *ibid.* 1059); but now the product, instead of being corundum, is the cubic and optically isotropic mineral *spinel* ($MgAl_2O_4$ but often with an excess of Al_2O_3). Attempts to produce a blue corundum (*i.e.* sapphire) had repeatedly failed until it was obtained by A. Verneuil (Compt. rend. 1910, **150**, 185) by the addition of titanic oxide (TiO_2, 0·5%) and magnetic oxide of iron (Fe_3O_4, 1·5%). Analysis of this artificial sapphire gave: Al_2O_3 99·83–99·85%, TiO_2 0·11–0·13%, Fe_2O_3 trace; sp.gr. 3·977–4·01 (A. J. Moses, Amer. J. Sci. 1910, **30**, 271). A peculiar stone which has been sold as " synthetical alexandrite," exhibits, like the true alexandrite (a variety of chrysoberyl, $BeAl_2O_4$, *q.v.*) a green colour by daylight and a red colour by lamplight; this is in reality artificial corundum, and the change in colour may be attributed to the presence of colloidal chromic oxide (as suggested in the case of alexandrite by O. Hauser, Z. angew. Chem. 1910, **23**, 1464).

Besides being faceted as gem-stones, this artificial corundum is extensively used for watch jewels and the pivot supports of electric meters and other instruments. For this purpose it is more uniform in character and more reliable than the natural mineral (*see* Collected Researches, National Physical Lab. 1931, **24**, No. 1).

Minute crystals of beryl were prepared by P. Hautefeuille and A. Perrey in 1888 and by H. Traube in 1894; and more recently hexagonal prisms up to 2 cm. long and of a good emerald-green colour have been prepared by the I. G. Farbenind. A.-G. in Bitterfeld. This artificial emerald has been given the trade-name "*Igmerald*," but it has been produced in only limited amounts. The process of manufacture has not been disclosed; but as the crystals contain minute liquid enclosures with bubbles, the method is no doubt hydrothermal (M. Jaeger and H. Espig, Deut. Goldschmiede-Ztg. 1935, **38**, 347; H. Espig, Z. Krist. 1935, **92**, 387).

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On the artificial production of minerals in general, *see* L. Bourgeois, "Reproduction artificielle des minéraux," Paris, 1884 (Encycl. chim. de Frémy); P. Tschirwinsky, "Reproduction artificielle de minéraux au XIX^e siècle," Kieff, 1903–6; G. W Morey and E. Ingerson, Econ. Geol. 1937, **32**, 607; E. H. Kraus and C. B. Slawson, "Gems and Gem Materials," 3rd ed., New York and London, 1939.

L. J. S.

GEMS, IMITATION AND COUNTERFEIT. As pointed out in the preceding article, it is necessary to distinguish between artificial (*i.e.* artificially produced) gems and imitation and counterfeit gems. Owing to their rarity and high value, gem-stones have been imitated in various kinds of material since very early times. For instance, although a few of the ancient Egyptian scarabs were cut in genuine turquoise, the great majority of them were made of a blue pottery or faience; and amongst the Romans, coloured glass was used for the imitation of the various transparent coloured gem-stones.

The material most extensively used for the manufacture of imitation gems is a heavy lead (flint) glass known as *paste* or *strass*. This is prepared by fusing in a crucible a mixture of powdered rock-crystal (SiO_2, 38–59%), red lead (Pb_3O_4, 28–53%), potassium carbonate (K_2CO_3, 8–14%), together with a small proportion of borax, white arsenic or saltpetre. Different recipes vary widely, the amount of lead present depending on the refractive index of the gem to be imitated. A dense flint-glass of sp.gr. 3·54 (*i.e.* about the same as diamond) has n_D=1·6118 and dispersion $n_{G'}-n_{A'}$=0·0315; and an extra-dense flint-glass of sp.gr. 5·004 has n_D=1·7784 and dispersion $n_{G'}-n_{A'}$=0·0568 (the corresponding values for diamond being 2·4173 and 0·0574 respectively). Optical values still higher are obtained by replacing the potassium by thallium; the sp.gr. of a thallium-lead glass may be as high as 5·6. To obtain the best results in the manufacture of strass, the materials employed must be quite pure; and the fusion carefully conducted, in order to avoid bubbles and streaks. Imitation diamonds (so-called "Parisian diamonds," etc.) are cut from the colourless paste. To prepare coloured pastes, the colourless paste is powdered, intimately mixed with various metallic oxides or other substances, and again fused. A blue colour is obtained with cobalt oxide; green, with cupric oxide or chromic oxide; red, with cuprous oxide, gold chloride or purple of Cassius; yellow, with silver chloride, antimony oxide or red antimony, or (in leadless glasses) with coal and a little manganese oxide; black, with tin oxide, manganese oxide and hammer-slag. An opaque white glass, or enamel, is obtained by the addition of tin oxide, calcium phosphate or bone-ashes; this may be suitably coloured to imitate opaque stones (*e.g.* turquoise) by the addition of metallic oxides.

These glasses often afford very clever imitations of the various precious stones, resembling them so closely, indeed, that without examination they may be readily mistaken for the genuine article. They are, however, all remarkable for their low degree of hardness, less than that of ordinary window-glass, and they can be readily scratched with a knife. In course of time they display a dark leaden tarnish on their surface, and when worn in jewellery their edges becomes rubbed and chipped. When examined with a magnifying-lens, bubbles and streaks are often to be seen in them. Optically they are isotropic and lacking in dichroism.

To avoid the effects of abrasion in wear, and also no doubt as a deception in case the test of hardness is applied, these soft materials are sometimes faced with a harder material such as rock-crystal or colourless topaz. In the *doublet*, the upper portion, above the girdle, consists of this harder, colourless material, while the lower portion, protected in the setting, consists of coloured strass which imparts its fine colour and brilliancy to the whole. The *triplet* consists of an upper and a lower portion of harder material, with a layer of the coloured strass between. Such counterfeits can, of course, be readily detected when the unmounted gem is viewed sideways, but when it is mounted in its setting detection is not so easy. Doublets and triplets are also built up of genuine stones, with the object of improving the colour, and of producing a gem of larger size.

Another kind of fraud sometimes practised with precious stones is the substitution of less valuable stones for more valuable. Unfortunately, the nomenclature of gems, as adopted by jewellers, offers an opening in this direction. Thus stones of a red colour are often known collectively as ruby with some qualifying prefix: *e.g.* "spinel-ruby" (= spinel), "Cape ruby" (= pyrope garnet), and "Siberian ruby" (= tourmaline), the true ruby ("Oriental ruby" of jewellers) being, of course, corundum; or again, "Oriental emerald" (= corundum), "Uralian emerald" (= demantoid garnet), "lithia-emerald" (= spodumene) and "Brazilian emerald" (= tourmaline), the true emerald being beryl of a grass-green colour. In the same way, yellow quartz ("Spanish topaz" or "Occidental topaz") is often mistaken for and sold as topaz. Other deceptive terms of a like nature are "Marmorosch diamonds," "Cornish diamonds," "Bristol diamonds," etc., for small sparkling crystals of quartz; and "Matura diamonds" (from Matura in Ceylon) for zircon of a brilliant lustre, which has been decolorised by the application of heat. The latter, as well as colourless corundum ("white sapphire"), have occasionally been passed off as diamonds.

Other attempts have been made to produce gems of much the same chemical composition as the genuine stones. For example, green glass with the composition of emerald. Very successful imitations of turquoise have been obtained by submitting to pressure a precipitate having the same composition as the natural mineral.

The artificial colouring of natural stones is also extensively practised. Almost all cut agates have been so treated (*v.* AGATE). Chalcedony can be so cleverly coloured a delicate green with salts of nickel or chromium, as to be practically indistinguishable from the more expensive chrysoprase. A pale-coloured jasper or hornstone, quarried at Nunkirchen, near Merzig, in Rhine Province, is coloured artificially by soaking first in a solution of ferrous sulphate and afterwards in one of potassium ferrocyanide. Beads and other small ornaments of this material are cut at Oberstein and are sold in large quantities as "lapis-lazuli," "Swiss lapis" or "German lapis." It is readily distinguished from true lapis-lazuli by its greater hardness, and by the presence of small patches of crystalline quartz, which does not take this colour, and by the absence of specks of pyrite. The colour of many gem-stones can be changed by heating or by exposure to the emanations of radium. A trick of the meanest kind is to smear violet ink or other bluish colouring matter on the surface of a yellowish (' off-coloured ") diamond, so giving it the appearance of a colourless gem.

References.—M. Bauer, "Precious Stones," English transl. by L. J. Spencer, 1904; M. Bauer, "Edelsteinkunde," 3rd ed. by K. Schlossmacher, Leipzig, 1928–32; J. Escard, "Les Pierres précieuses," Paris, 1914.

J. L. S.

GEMSBOK BEANS. The seeds of *Bauhinia esculenta,* Birch. The plant is indigenous to South Africa and the seeds are said to be eaten both by natives and animals in the South-West Protectorate of the Union. The reddish-brown beans are approximately ½ in. in diameter and 2 g. in weight. The hard outer husk comprises about half the total weight. Bray (Analyst, 1921, **46**, 401) gives the following analysis:

	Moisture.	Crude proteins.	Fat.	Carbohydrates.	Fibre.	Ash.	Nutrient ratio.	Food units.
Husks alone . .	8·5	2·5	0·2	67·2	19·8	1·8	1:27·1	74
Kernels alone .	4·0	32·8	41·6	17·2	1·3	3·1	1:3·4	203
Whole beans. .	6·2	18·0	21·3	41·6	10·4	2·5	1:5·0	140

The beans yield approximately 14% of a golden-yellow oil with an agreeable nutty odour and flavour, and showing the following characteristics, n_D^0 1·464, d_{15}^{15} 0·9211, acid value 0·6, saponification value 190·0, iodine value 95·6, unsaponifiable matter 0·8%.

The residual cake after expression of oil has the composition, water 6·4, protein 52·2, fat 7·0, carhohydrates 27·4, fibre 2·1, ash 4·9%.

The seeds are free from alkaloids and cyanophoric glucosides.

A. G. Po.

GENESERINE (*v.* Vol. II, 199*d*).

GENESTROLE (*v.* Vol. IV, 189*a*).

GENISTEIN (*v.* Vol. IV, 189*a*).

GENISTIN (*v.* Vol. IV, 189*d*).

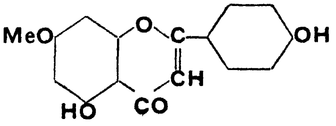
GENKWANIN. From the flowers of *Daphne genkwa,* Sieb. and Zucc., Nakao and Tseng (J. Pharm. Soc. Japan, 1932, **53**, 83, 148; J. Shanghai Sci. Inst. 1933, **1**, 1) isolated benzoic acid, sitosterol and the flavone derivatives apigenin and genkwanin.

Apigenin, for which Nakao and Tseng give m.p. 352°, also occurs as the glucoside *apiin* (*q.v.*) in the leaves, stem and seeds of parsley, from which source it was isolated by Perkin (J.C.S. 1897, **71**, 805) and shown to be 5:7:4′-trihydroxyflavone.

Genkwanin, $C_{16}H_{12}O_5$, yellow needles, m.p. 286°, contains one methoxyl group and on methylation yields 5-hydroxy-7:4′-dimethoxyflavone; it is thus an apigenin monomethyl ether, but is not identical with acacetin (5:7-dihydroxy-4′-methoxyflavone). When fused with potassium hydroxide it gives phloroglucinol and *p*-hydroxybenzoic acid, whereas with 50% potassium hydroxide solution, *p*-hydroxyacetophenone and phloroglucinol monomethyl ether are produced.

Genkwanin forms a *diacetyl* derivative, colourless needles, m.p. 196°, and a *dibenzoyl* compound, colourless needles, melting at 207–208°.

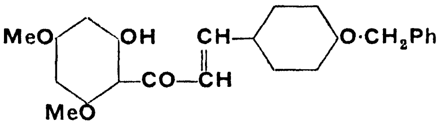
Nakao and Tseng suggested, therefore, that genkwanin is 5:4′-dihydroxy-7-methoxyflavone (I), and this formula has been confirmed by synthesis (Tseng, J. Pharm. Soc. Japan, 1935, **55**, 30). Phloracetophenone, when heated with *p*-benzyloxybenzoic anhydride and sodium *p*-benzyloxybenzoate, gives a product which on acetylation and subsequent hydrolysis furnishes 5:7-dihydroxy-4′-benzyloxyflavone. This compound is converted by methylation into 5-



I.

hydroxy-4′-benzyloxy-7-methoxyflavone from which genkwanin (I) is obtained by hydrolysis with alcoholic potassium hydroxide.

Genkwanin has also been synthesised (Mahal and Venkataraman, J.C.S. 1936, 569) by oxidising 2-hydroxy-4′-benzyloxy-4:6-dimethoxychalkone (II) by means of selenium dioxide to the corresponding flavone; debenzylation with hydrochloric acid in acetic acid gives genkwanin 5-methyl ether which is converted into genkwanin by partial demethylation with aluminium chloride.



II.

E. J. C.

GENTIAN. *Gentianæ radix,* British Pharmacopœia; *Gentiana,* United States Pharmacopœia; (*Racine de Gentiane,* Fr.; *Enzianwurzel,* Ger.). The dried root and rhizome of *Gentiana lutea* Linn. is widely used in medicine as a bitter tonic. The plant is a herbaceous perennial growing in the mountainous districts of Central and South-West Europe. The appearance and characteristic odour of the commercial drug are produced by fermentative changes which take place during drying. These changes modify the nature of the glycosides, on which the physiological action of the drug mainly depends. In the fresh state, gentian contains three glycosides, *gentiopicrin, gentiamarin* and *gentiin,* the total glycosidal content amounting to about 2%. As a result of enzyme action most, if not all, of the gentiopicrin is destroyed during drying, and the action of the drug is therefore due to gentiin and gentiamarin.

Gentiopicrin, $C_{16}H_{20}O_9$, is a crystalline lactone readily soluble in water. When anhydrous, it melts at 191°, but also forms a hemihydrate, melting at 122°. It is lævorotatory, the anhydrous substance having an optical activity of −204°. By the action of emulsin gentiopicrin is hydrolysed, forming dextrose and a crystalline, non-bitter substance, *gentiagenin,* $C_{10}H_{10}O_4$, m.p. 185°. A similar hydrolysis is brought about by acids, but the gentiagenin is attacked and an amorphous dehydration-product is finally formed.

Gentiamarin, $C_{16}H_{22}O_{10}$, or $C_{16}H_{20}O_{10}$, is an amorphous substance, very soluble in water and alcohol; it is not a lactone. On hydrolysis with acids, an amorphous brown substance is formed; with emulsin, dextrose and an amorphous maroon-coloured substance (Tanret, Bull. Soc. chim. 1905, [iii], **33**, 1071).

Gentiin, $C_{25}H_{28}O_{14}$, is probably the most important of the glycosides of commercial gentian. It occurs as micro-crystalline yellowish needles, almost insoluble in water, m.p. 274°, with decomposition. It dissolves in sulphuric acid to give a green-coloured solution. It hydrolyses slowly with 4% sulphuric acid, yielding dextrose, xylose and a crystalline substance, *gentienin,* $C_{14}H_{10}O_5$. When heated gentienin begins to sublime at 195° and melts at 225°. It is isomeric with *gentisin* (*v. infra*), but differs in melting-point, and in its behaviour with nitric acid, with which it gives a yellow colour.

The glycosides of gentian were first obtained by Kromayer (Arch. Pharm. 1862, **110**, 27 who isolated about 0·14% of gentiopicrin from the fresh root. Tanret (Bull. Soc. chim. 1905, [iii], **33**, 1059), Bourquelot and Bridel (J. Pharm. Chim. 1910, [vii]), **1**, 156) and Bourquelot and Hérissey (Compt. rend. 1900, **131**, 113) also gave methods for extracting and separating the glycosides. The following method may be used: the fresh root is finely cut and extracted with boiling alcohol, which destroys enzymes and extracts the glycosides without decomposition. The residue from the alcoholic extract is exhausted by repeated extraction with ethyl acetate saturated with water. The ethyl acetate extracts are evaporated to a syrup, which on standing deposits a crystalline mass. This is dissolved in alcohol. On cooling, crude gentiopicrin crystallises out, and is purified by recrystallisation either from a mixture of chloroform and 95% alcohol in equal parts, or from moist ethyl acetate solution. Gentiin may be obtained from the mother-liquors from which the purified gentiopicrin has been separated. The residue from these liquors is extracted with water, and the water-insoluble fraction dissolved in 60% alcohol. From this solution gentiin crystallises on cooling. Gentiamarin may be obtained from the alcoholic mother-liquors from which the crude gentiopicrin separates. The residue from these liquors is washed with ether, then with chloroform, and the insoluble portion dissolved in water. Tannin is added in excess, the resulting precipitate filtered off and rejected, and the filtrate saturated with magnesium sulphate. The precipitate, after washing with magnesium sulphate solution, is extracted with 80% alcohol, the alcoholic solution is purified by treatment with litharge, excess of lead removed by sulphuric acid and the filtrate evaporated. Any gentiopicrin remaining in the mother-liquors crystallises out on cooling, and is removed, leaving the gentiarmarin in solution, from which it may be obtained by evaporation. Other constituents of gentian are *gentisin pectin,* and the trisaccharide, *gentianose.*

Gentisin (*q.v.*).

Pectin is present in gentian root in large proportion. This yields mucic acid on oxidation by dilute nitric acid and arabinose on hydrolysis with dilute sulphuric acid (Bourquelot and Hérissey, J. Pharm. Chim. 1897, [vi], **8**, 49). Fermentable sugar is present in so large a proportion that it has led to the root being employed in Switzerland and Bavaria in the manufacture of spirit. Investigations carried out by Bourquelot and his co-workers (Bourquelot and Nardin, Compt. rend. 1898, **126**, 280; Bourquelot and Hérissey, *ibid.* 1900, **131**, 750; 1902, **135**, 290) show that fresh gentian root contains *gentianose,* a hexatriose, $C_{18}H_{32}O_{16}$, which melts at 207–209°, and is dextro-rotatory. It does not reduce Barreswil's (Fehling's) solution, but, if boiled with dilute sulphuric acid or acted upon by invertase, it becomes lævorotatory, and acquires considerable reducing power, having become hydrolysed into lævulose and a new hexabiose, *gentiobiose*, which, by more vigorous treatment, can be hydrolysed into 2 mol. of glucose. For derivatives, *see* Hudson and Johnson, J. Amer. Chem. Soc. 1917, **39**, 1272. For the detection of gentian-bitter in beer, *see* Dragendorff (Chem. Zentr. 1881, 285, 299); Allen (Analyst, 1887, **12**, 107; 1888, **13**, 43).

Other species of gentian which are claimed to have similar activity are *G. purpurea*, *G. punctata*, *G. pannonica*, *G. asclepiadea*, *G. cruciata*. In India, Azadirach (Neem bark), the dried stem bark of *Melia azadirachta* Linn. is usually employed as an equivalent of gentian.

The constituents of gentian are stated to undergo seasonal variation (Bridel, J. Pharm. Chim. 1911, [vii], **3**, 294). Gentiopicrin, 2% slightly increased in June and July; gentianose 3–5%, maximum in September, in May and June it is replaced by gentiobiose.

A. D. P.

GENTIANIN, an anthocyanin isolated from the petals of the common blue gentian (*Gentiana acaulis*). The pigment is extracted from the petals by means of methyl-alcoholic HCl, precipitated as the lead salt and purified through the *picrate*. The *chloride*, $C_{30}H_{27}O_{14}Cl$, dissolves in methyl alcohol containing a few drops of HCl with a bluish-red colour (rather bluer than delphinidin, *q.v.*), which becomes blue on adding either aqueous sodium carbonate or sodium hydroxide. Ferric chloride added to an aqueous solution of the *chloride* gives a blue colour, but in alcoholic solution the colour is violet-blue. Hydrolysis by means of cold $2N$-NaOH affords *p*-hydroxy-cinnamic acid (1 mol.), whilst hydrolysis with boiling 20% HCl gives delphinidin (1 mol.) and glucose (1 mol.). Gentianin is thus a *p*-hydroxycinnamoyl-delphinidin monoglucoside (Karrer and Widmer, Helv. Chim. Acta, 1927, **10**, 67).

W. B.

GENTIANOSE (*v.* Vol. II, 301*c*).

GENTIOBIOSE (*v.* Vol. II, 299*b*).

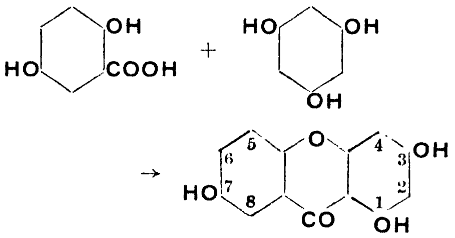
GENTISIC ACID (this Vol. p. 53*a*).

GENTISIN, the colouring matter of gentian root, was first isolated by Henry and Caventou (J. Pharm. Chim. 1821, 178), and was shown to possess the formula $C_{14}H_{10}O_5$ by Baumert (Annalen, 1847, **62**, 106) who prepared it by extracting the washed root with alcohol and concentrating the extract. The residue was washed with water to remove the bitter principle, then with ether to extract plant wax, and the crude colouring matter repeatedly crystallised from alcohol (yield, about 4 g. from 10 kg. of the root). Gentisin crystallises in yellow needles which darken at about 200° and sublime with decomposition between 300° and 340°. It is sparingly soluble in alcohol and dissolves in alkaline solutions with a yellow colour.

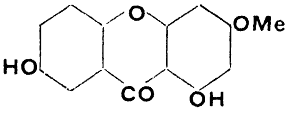
Hlasiwetz and Habermann (*ibid.* 1875, **175**, 63; 1876, **180**, 343) found that gentisin contains two hydroxyl groups, and when fused with potassium hydroxide yields phloroglucinol and gentisic acid (2:5-dihydroxybenzoic acid).

Gentisein. When gentisin is digested with boiling hydriodic acid, it is converted into gentisein with evolution of 1 mol. of methyl iodide. Gentisein forms straw-yellow needles melting at 315° (von Kostanecki, Monatsh. 1891, **12**, 205. Shinoda, J.C.S. 1927, 1983, gives m.p. 318° after darkening at 310°). It gives with sodium amalgam a blood-red coloration, whereas gentisin, by a similar method, yields a deep green liquid. With acetic anhydride, gentisein yields a *triacetyl* derivative, needles, m.p. 226° (von Kostanecki, *l.c.*), and on methylation with methyl iodide, a *dimethyl ether*, yellow needles, m.p. 167°, is produced (von Kostanecki and Schmidt, Monatsh. 1891, **12**, 318).

von Kostanecki and Tambor (*ibid.* 1894, **15**, 1) synthesised gentisein by distilling a mixture of phloroglucinol and 2:5-dihydroxybenzoic acid with acetic anhydride, and thus proved it to be 1:3:7-trihydroxyxanthone:



Partial methylation converts gentisein into gentisin, and it is thus certain that the latter is gentisein monomethyl ether. From the behaviour of *bisbenzeneazogentisin*, scarlet needles, m.p. 251–252°, which gives the *diacetyl* derivative, orange-red needles, m.p. 218–220°, Perkin (J.C.S. 1898, **73**, 672) concluded that gentisin possesses the constitution (I). As gentisin yields



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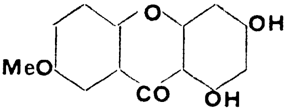


II.

only a monomethyl ether with methyl iodide, the original methoxyl group cannot be in the 1-position, *i.e.* adjacent to the carbonyl group. On the other hand, if gentisin is represented by formula (II), the azobenzene groups would enter the positions 4 and 2, and from such a compound an acetyl derivative cannot be obtained (*cf.* bisbenzeneazophloroglucinol). Again, Shinoda (*l.c.*) synthesised 1:3-dihydroxy-7-methoxyxanthone (II) and found it to be quite different from gentisin, thus confirming Perkin's view that gentisin is 1:7-dihydroxy-3-methoxyxanthone (I).

Nakaoki (J. Pharm. Soc. Japan, 1927, No. 540, 27) states that gentisin is present in the Japanese drug "To-Yaku" (from *Swertia japonica* Makino), but since the melting-point is given as 267°, this is doubtful.

Gentisin is a feeble dyestuff and gives on wool mordanted with chromium, aluminium and tin, pale green-yellow, pale bright yellow and very pale cream-coloured shades, respectively (Perkin and Hummel, J.C.S. 1896, **69**, 1290).

A. G. P. and E. J. C.

GEOCORONIUM (*v.* Vol. I, 539*a*).

GEODIN (*v.* this Vol. p. 58*b*).

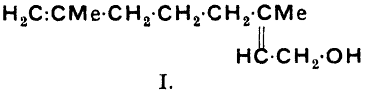
GEOFFROYINE. The name originally applied to the alkaloid *surinamine* (rhatanine), extracted from Geoffroya bark. It is identical with N-methyl-*l*-tyrosine (Fischer and Lipschitz, Ber. 1915, **48**, 360).

GEOSOTE (*v.* Vol. IV, 28*b*).

GERANIAL (*v.* Vol. III, 183*c*).

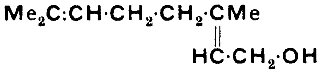
GERANIOL. The unsaturated primary alcohol, *geraniol*, $C_{10}H_{18}O$, b.p. 229–230°/757 mm., d^{15} 0·883, n_D^{20} 1·4763, occurs widely distributed in nature both in the free state and in combination. It forms the principal constituent of Palmarosa oil (from *Cymbopogon martini* Stapf var. *motia*). This oil is known also as Turkish geranium oil and *Rosha* or *Rosa* grass oil. Geraniol, is readily purified through the compound which it forms with calcium chloride (Jacobsen, Annalen, 1871, **157**, 234) and it can be characterised by its *diphenylurethane*, m.p. 82° (Erdmann and Huth, J. pr. Chem. 1896, [ii], **53**, 45; 1897, [ii], **56**, 28).

Geraniol has been shown to be a mixture of the two alcohols represented by (I) and (II), the composition of the mixture varying with the source and previous treatment of the oil; the *iso*propylidene form (II) is the main constituent of the natural alcohol (Grignard and Escourrou, Bull. Soc. chim. 1925, [iv], **37**, 542, 546; Grignard and Doeuvre, *ibid.* 1927, [iv], **41**, 999; Escourrou, *ibid.* 1928, [iv], **43**, 1091, 1211; Doeuvre, Parfums de France, 1934, **12**, 197).



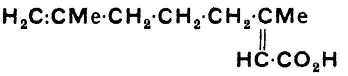
$$\begin{array}{l} H_2C{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe \\ \qquad\qquad\qquad\qquad\qquad\quad\ \| \\ \qquad\qquad\qquad\qquad\qquad HC{\cdot}CH_2{\cdot}OH \end{array}$$

I.



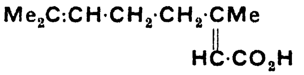
$$\begin{array}{l} Me_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe \\ \qquad\qquad\qquad\qquad\quad\ \| \\ \qquad\qquad\qquad\qquad HC{\cdot}CH_2{\cdot}OH \end{array}$$

II.



$$\begin{array}{l} H_2C{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe \\ \qquad\qquad\qquad\qquad\qquad\quad\ \| \\ \qquad\qquad\qquad\qquad\qquad HC{\cdot}CO_2H \end{array}$$

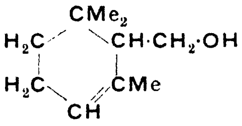
III.



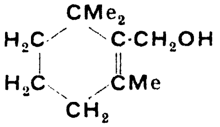
$$\begin{array}{l} Me_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe \\ \qquad\qquad\qquad\qquad\quad\ \| \\ \qquad\qquad\qquad\qquad HC{\cdot}CO_2H \end{array}$$

On oxidation with chromic acid geraniol yields the aldehyde, citral *a*, (Vol. III, 183*c*) together with the related acid, geranic acid (III). Since geraniol can be prepared by the reduction of citral *a* this comprises a complete synthesis of the alcohol. On oxidation with potassium permanganate geraniol gives as the main products acetone, formic and levulinic acids (*inter. al.*, Kötz and Steche, J. pr. Chem. 1924, [ii], **107**, 193). The products formed on catalytic hydrogenation depend upon the conditions used. It is possible to limit the reduction to one ethylenic linkage with the formation of citronellol (Paal, G.P. 298193; Grignard and Escourrou, *l.c.*; Grignard and Doeuvre, *l.c.*; Escourrou, *l.c.*). Further hydrogenation gives a mixture of the saturated alcohol, *tetrahydrogeraniol* (2:6-dimethyloctane-8-ol) and the related hydrocarbon, 2:6-dimethyloctane (Willstätter and Mayer, Ber. 1908, **41**, 1475).

Geraniol is stereoisomeric with nerol (*see below*) and it has the *cis*-configuration as represented in (I) and (II). By the action of dilute sulphuric acid it yields terpin hydrate, α-terpineol being an intermediate product, whilst with dilute phosphoric acid dipentene is obtained (Tiemann and Semmler, *ibid.* 1895, **28**, 2173; Bertram and Gildemeister, J. pr. Chem. 1894, [ii], **49**, 194; Zeitschel, Ber. 1906, **37**, 1780; Haarmann and Reimer, G.P. 138141). With formic acid a mixture of dipentene and terpinene is formed (Bertram and Gildemeister, J. pr. Chem. 1894, [ii], **49**, 194; 1896, [ii], **53**, 236). If geranyl acetate is treated with dehydrating agents (concentrated sulphuric or phosphoric acid) cyclisation occurs with the formation of acetyl *cyclo*geraniols (Haarmann and Reimer, G.P. 138141). The cyclic alcohol, obtained by the hydrolysis of the acetyl derivative, is a mixture of the α- and β-forms (IV) and (V), b.p. 95–100°/12 mm., d^{20} 0·935–0·955, n_D 1·48. With sulphuric acid as the dehydrating agent the β-form predominates whilst with phosphoric acid the reverse is the case. The composition of the mixture is best determined by oxidation to the aldehydes, α- and β-*cyclo*citrals and finally to the related *cyclo*geranic acids. Pure β-*cyclo*geraniol does not appear to have been prepared, but Bouveault (Bull. Soc. chim. 1910, [iv], **7**, 354) has described the pure α-form and has characterised it by its *phenylurethane*, m.p. 75°.



IV.



V.

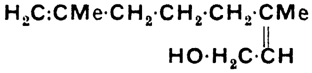
When geraniol is heated under pressure at 200° it is partly isomerised to the tertiary alcohol, linalool (Schimmel's Report, 1898, 25) and the same isomerisation occurs when geranyl hydrogen phthalate is subjected to distillation in steam (Stephan, J. pr. Chem. 1899, [ii], **60**, 252). If heated with concentrated alcoholic potassium hydroxide at 150° geraniol yields methylheptenol (VII), the primary product of the reaction, methylheptenone (VI), undergoing reduction (Barbier, Compt. rend. 1898, **126**, 1423; Tiemann, Ber. 1898, **31**, 2991). Like geraniol the ketone and alcohol are mixtures of the *iso*propenyl and *iso*propylidene forms:

$$\begin{array}{l}(\mathrm{I}) \rightarrow \mathrm{H_2C{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COMe} \\ \qquad\qquad\qquad\quad \downarrow \qquad\quad \mathrm{VI} \\ \qquad\quad \mathrm{H_2C{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}OH} \\ \qquad\qquad\qquad\quad \mathrm{VII.}\end{array}$$

$$\begin{array}{l}(\mathrm{II}) \rightarrow \mathrm{Me_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COMe} \\ \qquad\qquad\qquad\quad \downarrow \\ \qquad\quad \mathrm{Me_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}OH}\end{array}$$

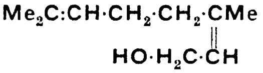
(Grignard and Doeuvre, *l.c.*).

Stereoisomeric with geraniol is the alcohol, *nerol*, the *trans*-modification, which is a mixture of (VIII) and (IX). This alcohol occurs in



$$\begin{array}{l}\mathrm{H_2C{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad \mathrm{HO{\cdot}H_2C{\cdot}CH}\end{array}$$

VIII.



$$\begin{array}{l}\mathrm{Me_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe} \\ \qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\quad \mathrm{HO{\cdot}H_2C{\cdot}CH}\end{array}$$

IX.

neroli, petitgrain, bergamot and a number of other essential oils. Nerol was first isolated by Hesse and Zeitschel (J. pr. Chem. 1902, [ii], **66**, 502), but the pure alcohol was first prepared by von Soden and Treff (Ber. 1904, **37**, 1094; 1906, **39**, 906) by the hydrolysis of its crystalline *diphenylurethane*, m.p. 52–53°. The alcohol has b.p. 225–226°, d^{15} 0·8813, and yields a crystalline *tetrabromide*, m.p. 116–118° On oxidation nerol gives citral *b* from which it can be prepared by reduction; it is more readily cyclised than geraniol but otherwise it has properties identical with those of this alcohol.

J. L. S.

GERANIOL (use in perfumes). This body, so largely employed in perfumery, is usually classed with synthetic perfumes, although the commercial article is invariably a natural isolate. It was first separated from Palmarosa oil (*Cymbopogon martini* var. *motia*) by Jacobsen (Annalen, 1871, **157**, 234), and has also been found in numerous other essential oils, notably in geranium, rose and citronella oils. As a commercial article geraniol occurs in various qualities which are of very different perfume and money values. The difference depends not on the absolute amount of true geraniol, but on the traces of impurities, which vary with the particular source from which the oil has been isolated.

The alcohol nerol, which occurs in the essential oils of neroli, petitgrain, bergamot and others, is isomeric with geraniol, it has a finer odour than geraniol and is more highly prized in the perfume industry.

Geraniol and its esters are used to a very considerable extent in the manufacture of artificial Otto of Rose, and in many perfumes where a rose note is required either as predominant in the perfume, or as a subsidiary modifier. The principal esters are the following:

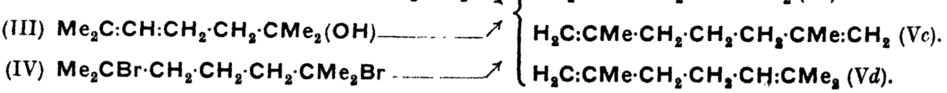
Ester.	B. esters.	Sp.gr. at 15·5°.	Ref. Index at 20°.
Geranyl formate	113°/15 mm.	0·924	1·4646
Geranyl acetate	244°	0·914	1·4625
Geranyl propionate	—	0·905	1·4600
Geranyl butyrate	—	0·902	1·4585
Geranyl valerate	—	0·892	1·4540

The above figures are necessarily approximate, as commercial samples vary slightly from the pure esters, which are not manufactured on a practical scale.

Geranyl Methyl Ether, $\mathrm{C_{10}H_{17}{\cdot}OMe}$, is a colourless oil prepared artificially, having a fruity odour recalling that of bergamot. It has sp.gr. 0·880–0·890 at 15·5°; is optically inactive, and boils at 208–212°.

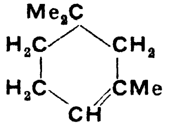
E. J. P.

GERANIOLENE. The hydrocarbon, *geraniolene*, $\mathrm{C_9H_{16}}$, b.p. 142–143°, d^{20} 0·757, n_D 1·4368, was prepared originally by Tiemann and Semmler (Ber. 1893, **26**, 2724) by the distillation of geranic acid (I). It was subsequently prepared (*a*) from hydroxydihydrogeranic acid (II) (Tiemann, *ibid.* 1900, **33**, 365); (*b*) by the dehydration of the alcohol (III) obtained by the action of methyl magnesium iodide on methylheptenone (Grignard, Thèse de Doctorat, 1901, 81); (*c*) by the elimination of hydrogen bromide from 2:6 - dibromo - 2:6 - dimethylheptane (IV) (Harries and Weil, Ber. 1904, **37**, 846).



$$\left.\begin{array}{l}(\mathrm{I})\ \mathrm{Me_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CO_2H} \searrow \\ (\mathrm{II})\ \mathrm{Me_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe(OH){\cdot}CH_2{\cdot}CO_2H} \searrow \\ (\mathrm{III})\ \mathrm{Me_2C{:}CH{:}CH_2{\cdot}CH_2{\cdot}CMe_2(OH)} \nearrow \\ (\mathrm{IV})\ \mathrm{Me_2CBr{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe_2Br} \nearrow \end{array}\right\{\begin{array}{l}\mathrm{Me_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2}\ (\mathrm{V}a). \\ \mathrm{Me_2C{:}CH{\cdot}CH_2{\cdot}CH{:}CMe_2}\ (\mathrm{V}b). \\ \mathrm{H_2C{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2}\ (\mathrm{V}c). \\ \mathrm{H_2C{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2}\ (\mathrm{V}d).\end{array}$$

The hydrocarbon prepared by these various methods is not homogeneous (Auwers and Eisenlohr, J. pr. Chem. 1910, [ii], **82**, 76; Auwers and Moosbrügger, Annalen, 1912, **387**, 183), but is a mixture of the isomerides (V*a*), (V*b*), (V*c*) and (V*d*), the actual percentage of each isomer present being dependent upon the method of preparation used. On treatment with sulphuric acid geraniolene yields cyclo*geraniolene*, b.p. 138–139°, d^{20} 0·8072, n_D 1·44731 (Tiemann and Semmler, Ber. 1893, **26**, 2724). The investigations of Tiemann (*ibid.* 1900, **33**, 3711), Wallach and Franke (Annalen, 1902, **324**, 114), Harries and Weil (Ber. 1904, **37**, 848), Crossley and Gilling (J.C.S. 1910, **97**, 2218) and of Escourrou (Bull. Soc. chim. 1926, [iv], **39**, 1460; 1928, [iv], **43**, 1277) have shown *cyclo*geraniolene to be a mixture of the *α*-, *β*- and *γ*-forms (VI), (VII) and (VIII). The *α*-form has been characterised by a crystalline *nitrosate*, m.p. 102–104°, and a *nitrosochloride*, m.p. 100–120°.



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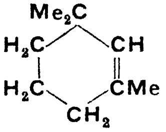
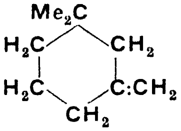


VII.



VIII.

J. L. S.

GERANIUM (artificial). For cheap perfumery, where a very delicate odour is not required, there are two synthetic products which satisfactorily reproduce the odour of geranium. These are diphenyl oxide, Ph_2O, white crystals, m.p. 28°, and diphenylmethane, Ph_2CH_2, colourless crystals, m.p. 26°, b.p. 260–261°, and d^{30}, 1·000.

E. J. P.

GERANIUM, ESSENTIAL OIL OF (Oil of Rose-Geranium). This oil is obtained by distillation from the leaves of various species of *Pelargonium* (Fam. Geraniaceæ) of which more than 160 species are known. These plants are natives of the dry rocky slopes of South Africa, but they are cultivated in Southern Europe, Northern Africa, Réunion and in other parts of the world. The odours of the various species differ considerably, but the majority have a strong rose odour on which the value of the oil depends. Three types of oil are found in commerce, French, Algerian and Bourbon, the market value of which depends largely on the crops although the French oil usually demands the highest price. Spanish oil of good quality is sometimes marketed.

Constituents.—The main constituents are geraniol and citronellol and their acetic, *iso*butyric, *iso*valeric and tiglic esters. Other constituents are *α*-terpineol, benzylcarbinol, menthol, menthone, linalool, phellandrene and traces of dimethyl sulphide. The mixed alcohols are known as *rhodinol* or *réuniol.*

Characters.	Sp.gr. at 15·5°.	Optical rotation $[\alpha]_D^{20}$.	Refractive index, n_D^{30}.	Esters calculated as geranyl tiglate, per cent.
French .	0·896–0·905	−6° to −10°	1·465–1·468	19–28
Algerian .	0·892–0·904	−6° to −12°	1·465–1·470	14–30
Bourbon .	0·888–0·896	−6° to −10°	1·461–1·466	21–33

All these oils are soluble in 3 vol. of 70% alcohol.

The proportion of citronellol is variable and attempts have been made to value the oil on the basis of this constituent. Various methods have been suggested and the formylation method proposed by Glichitch (Compt. rend. 1923, **177**, 268) has been found the most satisfactory.

C. T. B.

GERANIUM OIL, TURKISH OR INDIAN. A synonym for Palmarosa oil.

"*German Alloy*" (*v.* Vol. I, 253*a*).

GERMAN SESAMINE OIL (*v.* Vol. II, 237*a*).

GERMAN SILVER. An alloy of nickel with copper and zinc which is not readily corroded and may be worked in a variety of ways. Such alloys contain usually 55–60% of copper, 20–30% of zinc, and 15–20% of nickel, but lower grades may contain only 5–7% of the last metal.

GERMANITE. One of the very few minerals containing germanium as an essential constituent, and noteworthy also in containing an appreciable amount of gallium. It has been found only in one part of the Tsumeb mine in South-West Africa, but there in some quantity, being first noticed by H. Schneiderhöhn in 1916, and described and named by O. Pufahl in 1922. It occurs in the massive sulphide ore intimately intermixed with tennantite, enargite, pyrite, chalcosine, bornite, galena, and zinc-blende. Locally it has been known as "rose ore" because of its reddish-violet colour, which tarnishes on exposure to air. It has a dull metallic lustre, and gives a black streak. There is no cleavage; hardness 2½–3; sp.gr. 4·29. Polished sections in reflected polarised light show the mineral to be very fine grained and optically isotropic, and much veined with other minerals. X-ray powder photographs show it to be cubic with the same type of structure as zinc-blende and tetrahedrite. The unit cell of edge 5·290Å is assumed to contain 1 mol. of $Cu_3(Fe,Ge)S_4$ and the calculated density is 4·30. Owing to the intimate association with other minerals the few analyses of germanite show some variation, and the formula is uncertain. E. Thomson (1924) provisionally suggests $16Cu_2S\cdot 4GeS_2\cdot As_2S_3$, and H. Moritz (quoted by Schneiderhöhn and Ramdohr, 1931), from an analysis made on material bored out under the microscope from polished sections, gives

$$2Cu_2S\cdot(Zn,Fe,Ga)S\cdot(Ge,As)_2S_3.$$

ANALYSES OF GERMANITE.

	S.	Cu.	Fe.	Ge.	As.	Zn.	Pb.
I.	31·34	45·40	7·22	6·20	5·03	2·61	0·69
II.	30·53	43·80	6·27	8·71	4·12	2·69	1·74
III.	30·65	45·39	4·56	8·70	4·13	2·58	0·66
IV.	30·96	44·01	5·08	5·10	6·83	2·74	2·26
V.	31·44	39·44	10·70	7·04	4·86	3·56	0·26
VI.	31·27	42·12	7·80	10·19	1·37	3·93	0·96

I. O. Pufahl, Metall u. Erz, 1922, **19**, 324; also SiO_2 0·75, total 99·24.

II. F. W. Kriesel, *ibid.* 1923, **20**, 257; also Ga 0·74, Mo 0·03, Au,Ag 0·006, SiO_2 0·20, total 98·836

III. F. W. Kriesel, Chem.-Ztg. 1924, **48**, 961; also Ga 0·76, Mo 1·282, WO_3 0·184, TiO_2 0·004, Mn 0·02, Ni 0·001, Co 0·013, Cd 0·071, CaO 0·122, MgO 0·055, Ag,Au 0·005, C 0·136, SiO_2 0·226, total 99·549.

IV. J. Lunt, South African J. Sci. 1923, **20**, 157 (anal. J. S. Thomas); also Ga 0·57, W 0·03, Mo,Au traces, SiO_2 1·84, total 99·42.

V. E. Thomson, Univ. Toronto Studies, Geol. Ser. 1924, No. 17, p. 62 (anal. E. W. Todd); also SiO_2 1·68, total 98·98.

VI. H. Moritz, Neues Jahrb. Min. A, 1933, **67**, 118; also Ga 1·85, total 99·49; formula $Cu_8(Zn,Fe,Ga)_2 \cdot (Ga,As)_2S_{11-12}$.

Other references to germanite are:

J. S. Thomas and W. Pugh, J.C.S. 1924, **125**, 816. Here the hardness is given as 4, and sp.gr. 4·59.

W. F. de Jong, Z. Krist. 1930, **73**, 176. X-ray examination.

H. Schneiderhöhn and P. Ramdohr, Lehrb. d. Erzmikroskopie, Berlin, 1931, **2**, p. 441.

R. Berg and W. Keil, Z. anorg. Chem. 1932, **209**, 383. Analysis gave Ge 6·8, Ga 0·74%.

F. Sebba and W. Pugh, J.C.S. 1937, 1371. Analysis and extraction by a new method gave higher gallium, Ga 1·25%, with GeO_2 7·9%.

In addition to argyrodite (*q.v.*) in which the element germanium was discovered by C. Winkler in 1886, the only other mineral containing germanium as an essential constituent is one described under the name *ultrabasite*, by V. Rosický and J. Štěrba-Böhn (Rozpravy České Akad. Cl. 2, 1916, **25**, No. 45; Z. Kryst. Min. 1920, **55**, 430). This was detected on two small specimens from an old collection of minerals, which were labelled as coming from the Himmelsfürst mine at Freiberg, Saxony, the same mine that yielded the original argyrodite. The crystals are orthorhombic with a tetragonal habit; streak black, fracture conchoidal, hardness 5, sp.gr. 6·026. Analysis, S 16·15, Sb 4·60, Ag 22·35, Pb 54·16, Cu 0·47, Fe 0·25, Ge 2·20, total 100·18, gives the ultrabasic formula

$$Sb_4Ag_{22}Pb_{28}Ge_3S_{53}$$

Germanium has been detected spectroscopically in various minerals. In the tin minerals, cassiterite (Ge 0·005%), stannite, cylindrite, and franckeite. In zinc minerals, blende,[1] smithsonite (GeO_2 0·01%), and in the evaporated residue of mine water from Kentucky (GeO_2 0·29%). In copper minerals, enargite from Mexico (Ge 0·01%), native copper from Arizona (Ge 0·001%). In brookite from Moravia, and in fergusonite from Japan. In various silicates, topaz from Manitoba (GeO_2 0·001%), lepidolite, tourmaline, spodumene, and felspars. In gem white sapphire from Ceylon. In meteoric irons (Ge 0·01–0·1%) and meteoric stones.

L. J. S.

GERMANIUM (At. Wt. 72·6; At. No. 32). This element, the *eka-silicon* of Mendeléef, was discovered by Winkler[1] in 1886 in *argyrodite* (*q.v.*), a silver germanium sulphide,

$$GeS_2,4Ag_2S,$$

found in Freiberg in Saxony. It is also found in *canfieldite*, Ag_8SnS_6, a stanniferous argyrodite, and, to the extent of about 1%, in certain other Bolivian thiostannates such as *cylindrite* (*q.v.*) *franckeite* (*q.v.*) and *wolfsbergite*. It is also a constituent of *germanite* (*q.v.*) ("pink-eye") a dark reddish-grey mineral found in South-West Africa and which is mainly a copper-arsenic glance containing 4–10% of germanium. Zinc blendes, especially those of North America, often contain this element which is widely distributed in nature, traces being found in almost all magmatic rocks and minerals as well as meteorites. Like certain other metals it is concentrated to some extent in coal and is therefore found in coal ash and flue dusts which may contain up to 1·5% of germanium.[72, 150]

Extraction of the metal is usually accomplished in one of the following ways:

(*a*) By suitable decomposition of the mineral, preceded in some cases by roasting to remove part of the arsenic and sulphur, followed by heating with hydrochloric acid whereby the volatile tetrachloride is distilled and collected. If arsenic is present distillation is performed in a current of chlorine which maintains this element in its less volatile quinquevalent state. The germanium tetrachloride is converted to the dioxide either through the sulphide or by hydrolysis, the product being reduced with hydrogen at 900°. The resulting metallic powder may be rendered massive by fusing under sodium chloride or, alternatively, the oxide may be reduced with charcoal under sodium chloride or with potassium cyanide.[7, 9, 10, 18, 19, 21, 33, 42, 52, 62, 64]

(*b*) By heating the material at 900–1,000° with sulphur or with hydrogen sulphide in a reducing atmosphere when germanous sulphide sublimes and is collected and roasted to the dioxide (B.P. 378017). From germanite GeS may be obtained by the action of ammonia alone.[139]

PHYSICAL PROPERTIES.—The compact metal is greyish-white, brittle and highly lustrous; fused under salt it possesses a fine crystalline structure, the surface consisting of aggregates of elongated crystals. The lattice is of the diamond type and there is no indication of allotropic transformations between 20° and 1,100°K.[19, 156] It melts at 958·5°; published values for the boiling-point lie between 1,900° and 2,700°. Germanium displaces silver from silver nitrate solutions while it may be deposited electrolytically on copper from alkaline solutions or, together with tin, from alkaline oxalate solutions.[121, 145] Aston[53] assigns 8 isotopes to germanium (^{70}Ge to ^{77}Ge) but Bainbridge[111] states that the 71, 75 and 77 lines are due mainly, if not entirely, to hydrides of ^{70}Ge, ^{74}Ge and ^{76}Ge. Other physical properties are:

Density,[19, 80] d^{20}_{20} 5·35; d^{20} 5·302.

Hardness,[19] 6·25 on Mohs' scale.

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[1] A spectroscopic estimation of Ge 2–4% in zinc-blende from near Aberysthwyth, Wales (W. Scutt, Phil. Mag. 1926 [vii] **1**, 1007), surely requires confirmation; and of Ge 1–3% in pyragyrite from Colquechaca, Bolivia (J. Papish, Econ. Geol. 1928, **23**, 660) is no doubt due to the presence of associated argyrodite.

Compressibility,[20]

$$K \times 10^7 = -(13{\cdot}78 - 6{\cdot}8 \times 10^{-5} p)$$

at 30° for pressures (p) up to 12,000 kg. per sq. cm.

Critical constants,[8] $T_c = 4{,}170°$; $P_c = 910$ atm.

Specific (atomic) heats,[3, 122] mean values, 0–100° = 0·0737(5·33), 0–211° = 0·773(5·59), 0–300° = 0·0768(5·65), 0–440° = 0·0757(5·47).

Parachor,[94] [P] = 37·4.

Magnetic susceptibility,[6]

$$\chi(30°) = -0{\cdot}118 \times 10^{-6}.$$

Specific resistance,[11] $r = 0{\cdot}089$ ohm. per cm. at 0°.

Spectrum.[46, 51, 54] The most intense lines are as follows:

Arc: 2,417·37, 2,592·54, 2,651·19, 2,651·57, 3,039·07, 3,269·51, 4,226·60.

Spark: 2,592·65, 2,651·29, 2,651·69, 2,709·69, 2,754·68, 3,039·20, 4,179·20, 4,226·76, 4,686·09.

For spectral series, *see* Rao and Narayan,[59] Rao,[60] Lang,[66] Gartlein[85] and Smith.[47]

CHEMICAL PROPERTIES.—Belonging to the fourth group of the Periodic Table germanium comes between silicon and tin; it resembles the latter in forming two series of compounds in which it is respectively bi- and quadri-valent while its relationship to silicon is seen in the hydrides and halides, in the formation of glasses resembling fused quartz and the crown and flint glasses and in the high melting and boiling-points of the metal. Germanium is a comparatively stable element unaffected by moist or dry air up to 600° although above this temperature oxidation begins. It is not attacked by hydrogen up to 1,000°, and, in the massive form, is not affected by halogens at room temperatures; the finely divided metal burns in chlorine and bromine. Hydrogen peroxide slowly oxidises it, the reaction being fairly rapid at 90°. Germanium is only slowly acted upon by mineral acids, hot or cold, although aqua regia readily dissolves it. Heated in hydrogen chloride it forms germanochloroform. Sulphur vapour attacks heated germanium yielding the monosulphide, but hydrogen sulphide has little effect below its dissociation temperature; with sulphur dioxide above 500° there is produced a mixture of dioxide and disulphide. The metal readily dissolves in fused alkalis, alkali peroxides, nitrates or carbonates.

For the analytical chemistry of germanium, *see* CHEMICAL ANALYSIS, II, 555*a*, 571*a*, 595*c*.

ALLOYS OF GERMANIUM.

These have received comparatively little study and the number of intermetallic compounds formed is small.

Sodium.—By heating equiatomic proportions of the elements at 1,000° in the absence of air there is formed a hard pyrophoric mass of *sodium germanide*, $NaGe$, which is decomposed by moist air.[74]

Copper.—The germanium-copper system shows several series of mixed crystals and also a *compound*, Cu_3Ge; which forms a eutectic with germanium at 650° and 35 atomic per cent. Ge. The alloys vary in colour with increasing germanium content from golden-yellow to greyish-white and they are harder but more brittle than copper. Aqua regia attacks all the alloys and nitric acid those containing more than 75% Cu; they are untouched by hydrochloric acid and only slowly affected by boiling sulphuric acid.[124]

Silver.—No stable compounds appear to be formed but only a solid solution; the alloys form a simple eutectic series the eutectic being at 650° and 74 atomic per cent. Ag.[67]

Magnesium.—Heated together in hydrogen in the correct proportions the metals form a brittle dark grey *magnesium germanide*, Mg_2Ge, which generates germanium hydrides with acids.[12, 23]

Mercury.—Germanium is but slightly soluble in mercury and amalgam formation is only observable above 250°; the resistivity of the amalgams is less than that of mercury at the same temperature.[34]

Aluminium.—No compounds and no solid solutions are formed although all alloys show the presence of a eutectic containing 29·5 atomic per cent. Ge, m.p. 424°. Their hardness increases with the germanium content and is greater than for the corresponding silicon-aluminium alloys.[161] Germanium may replace silicon in alloys of the duralumin type.[35]

Lead.—Neither solid solutions nor eutectic is observed, the germanium separating completely on cooling the melt.[73] The behaviour with *tin* appears to be similar.[151]

Tellurium.—A *compound* $GeTe$ is formed, m.p. 725°, d^{25} 6·20 which is not readily acted on by acids other than aqua regia.[125]

Uses.—Little use has, as yet, been made either of the metal, its alloys or derivatives. Its sulphide has been suggested as a hydrogenation catalyst while zinc or magnesium orthogermanate has been proposed as a luminescent material in the fluorescent screens of cathode-ray tubes (B.P. 414905). Some of its derivatives may prove useful in anæmia although they appear to have little value against experimental infections.[148]

COMPOUNDS OF GERMANIUM.

With Hydrogen.—Germanium solutions when reduced electrolytically or by means of sodium amalgam or aluminium and dilute alkali evolve a gas with an unpleasant odour and which burns with a bluish-red flame. Passing the gas through a heated tube or inserting a cold surface into the flame causes the deposition of a metallic film or mirror which is soluble in sodium hypochlorite.[5, 13, 14, 15, 26, 135] On an analogy with arsenic the gas was presumed to be *germanium hydride* (*monogermane, germanomethane*), GeH_4, and this was confirmed by passing it into silver nitrate solution when a black germanium-silver complex was deposited.[5, 15] Monogermane is also produced by treating zinc or magnesium alloys of germanium with sulphuric or hydrochloric acids or by the action of ammonium bromide in liquid ammonia on magnesium germanide.[126] It boils about −90°, solidifies at −165° while the molecular weight from the vapour density is 76·66 ($GeH_4 = 76{\cdot}63$).

The gas produced above contains not only monogermane but also *digermane* (*germanoethane*), Ge_2H_6, and *trigermane* (*germanopropane*), Ge_3H_8; these are separated by fractional distillation of the liquid obtained by cooling the mixed gases in liquid air. Digermane is a colourless liquid, b.p. 29°, m.p. −109°, $d_{liq.}$ 1·98. Exposed to air it gradually forms a dark brown solid; under certain conditions the reaction may be so accelerated as to cause emission of light. It is insoluble in water which, however, slowly attacks it, producing in the aqueous layer a white precipitate becoming yellow and then brown; with caustic soda (33%) a combustible gas is evolved.

Trigermane is also a colourless liquid, b.p. 110·5°, m.p. −105·6°, $d_{liq.}$ 2·20; it forms a white solid in air but is unaffected by caustic soda solution.[23, 158]

Monogermane reacts with sodium in liquid ammonia to form sodium trihydrogermanide, NaH_3Ge, *a white solid crystallising with 6 mol.* of ammonia which are lost in stages; with oxygen the germanide yields sodium metagermanate while on standing it readily evolves hydrogen leaving sodium germanide, $NaGe$. This is probably the same as the product formed by heating the elements in the absence of air and which gives with water a dark brown powder, *germanium monohydride*, $(GeH)_x$; the latter decomposes slowly on drying in the absence of air and readily in its presence.[74, 126]

Acid hydrolysis of calcium germanide produces a *germanium dihydride*, $(GeH_2)_x$. This amorphous, non-volatile, yellow solid reacts explosively with oxygen forming water and the metal while sodium hydroxide successively replaces H by OH. Bromine oxidises it to the tetrabromide but halogen acids produce germanous halides together with mono-, di- and trigermane formed by reduction of some of the dihydride by the liberated hydrogen.[112]

HALOGEN DERIVATIVES OF GERMANIUM.

Germanous Fluoride, GeF_2.—Reduction of the tetrafluoride with germanium at 100–350° yields a white hygroscopic sublimate stated to be the difluoride, for its aqueous solution has reducing properties and deposits germanous sulphide on acidification and treatment with H_2S. Heated above 350° it reproduces the tetrafluoride and germanium.[2, 48]

Germanic Fluoride, GeF_4.—A solution of germanium dioxide in hydrofluoric acid when evaporated over sulphuric acid slowly deposits white crystals of the *trihydrate*, $GeF_4,3H_2O$, which is readily soluble in, and hydrolysed by, water.[2, 4] The anhydrous fluoride is a colourless fuming gas forming no liquid phase at ordinary pressure; in liquid air it condenses to a white crystalline solid which sublimes on raising the temperature. It is best made by heating barium germanifluoride at 700°, condensing the product in liquid air and fractionating in a vacuum apparatus.[48] Liquid GeF_4 is formed at −15° under its own vapour pressure of 3,032 mm., $d_{liq.}^{-16·5°}$ 2·40, $d_{solid}^{-195°}$ 3·148; the vapour density (6·71 g. per litre at 21°C. and 756·4 mm.) shows the absence of polymerised molecules.[102, 113] Germanic fluoride dissolves in water to a clear acid solution which slowly deposits the dioxide; addition of potassium hydroxide to the clear solution precipitates *potassium germanifluoride*, K_2GeF_6. Germanifluoric acid has not been isolated but many of the salts have been made of which the alkali and barium ones are sparingly soluble and slowly hydrolysed in water.[116]

Germanium Chlorofluorides.—The *chlorofluorides*, $GeClF_3$, $GeCl_2F_2$ and $GeCl_3F$ are formed when $GeCl_4$ is acted on by antimony trifluoride in the presence of antimony pentafluoride as catalyst. The first two are gases boiling at −20·3° and −2·8° and solidifying at −66·2° and −51·8° respectively while $GeCl_3F$ is a liquid with b.p. 37·5° and m.p. −49·8°. They are hydrolysed in moist air more readily than germanic chloride and tend to rearrange into this substance and the tetrafluoride.[143]

Chlorogermanes.—Hydrogen chloride and monogermane react in the presence of anhydrous aluminium chloride to produce *monochloromonogermane*, GeH_3Cl, and *dichloromonogermane*, GeH_2Cl_2, as mobile colourless liquids boiling respectively at 28° and 69·5°. They decompose slowly at ordinary temperatures, fume in moist air, and, on hydrolysis, give germanous oxide, hydrochloric acid and hydrogen. With absolute alcohol a white precipitate is formed.[65, 116]

Trichloromonogermane (Germanochloroform), $GeHCl_3$.—Gently heated germanium reacts exothermically with hydrogen chloride whereby hydrogen is liberated and a condensate produced which, according to Winkler, consisted of $GeHCl_3$ and the oxychloride, $GeOCl_2$, these being separated by distillation. Later work has shown that the tetrachloride is also formed and cannot be removed from the $GeHCl_3$ by distillation. The trichlorogermane is therefore obtained by the action of hydrogen chloride on germanous chloride[37]; it is a colourless liquid, b.p. 75·2°, m.p. −71°, d^0 1·93; it fumes in moist air and forms with a little water a white solid while larger amounts produce the orange germanous oxide. Above 140° it decomposes first into the dichloride and then into tetrachloride and germanium. Electrolysis of a solution in $7N$-HCl produces either germanous oxide or a solution of bivalent germanium.[152] With oxygen the following reaction is said to take place:

$$4GeHCl_3 + O_2 = 2GeCl_4 + 2GeCl_2 + 2H_2O$$

although Winkler believed that $GeOCl_2$ was formed. This *oxychloride* is, however, made by passing the vapour of germanochloroform over silver oxide; it is a colourless liquid, m.p. −56° insoluble in inorganic and organic solvents, and decomposing at 110° into GeO and chlorine.[104] For the Raman spectrum of $GeHCl_3$, *see* Volkringer and others.[131]

Germanous Chloride, $GeCl_2$.—Formed as an intermediate in the thermal decomposition of germanochloroform, it is best obtained by heating the metal at 350° in the vapour of germanic chloride, this reaction being reversed on heating the product above 75° *in vacuo*. The light yellow solid is insoluble in alcohol, chloroform or water, but the last medium slowly hydrolyses it to the monoxide. Chlorine oxidises it to the tetrachloride, hydrogen chloride gives trichloromonogermane while bromine produces a mixture of tetrachloride and tetrabromide; dry oxygen slowly generates the tetrachloride and dioxide.[63] On mixing hydrochloric acid solutions of germanous and rubidium or cæsium chlorides there are precipitated the *germanochlorides*, $\mathrm{Rb[GeCl_3]}$ and $\mathrm{Cs[GeCl_3]}$; double salts with quinine and pilocarpine hydrochloride are also known.[86]

Germanic Chloride (Germanium tetrachloride), $\mathrm{GeCl_4}$.—Obtained by heating the metal in chlorine,[1,16,36] the dioxide in phosgene,[40] or by distilling a solution of the dioxide in concentrated hydrochloric acid and separating the heavy layer of tetrachloride from the acid.[30,52] The product, after fractionation and removal of any chlorine or hydrogen chloride by the passage of dry air, is a colourless limpid liquid, b.p. 83·0°, m.p. −50°, d^{20}_{20} 1·879, refractive index n^{27}_{D} 1·4602, vapour density at 301·5°=7·45 ($\mathrm{GeCl_4}$=7·43). The critical pressure is 38 atm., critical temperature 276·9° and dielectric constant at 30° is 2·65; the dielectric behaviour shows a zero moment and a probable symmetrical tetragonal structure for the molecule.[127,132,138]

The tetrachloride fumes in moist air and is easily hydrolysed by water; it is soluble in many organic solvents and almost insoluble in hydrochloric and sulphuric acids; the latter acid has no effect on it while nitric acid only slowly attacks it. Alkalis react vigorously giving clear solutions from which carbon dioxide precipitates germanium dioxide. With dry ammonia there is formed a mixture of germanium imide and ammonium chloride, a light white powder slowly attacked by water.[40] Heated with oxygen at 900° the tetrachloride yields an *oxychloride*, $\mathrm{Ge_2OCl_6}$, b.p. 70°/13 mm.[89]

Bromogermanes.—*Monobromomonogermane* and *dibromomonogermane* are colourless liquids resembling the chloro derivatives and prepared similarly. The former has b.p. 52°, m.p. −32°, $d^{29\cdot5}$ 2·34 and the latter b.p. 89°, m.p. −15°, d^{0} 2·80.

Germanobromoform, $\mathrm{GeHBr_3}$.—Formed by the action of hydrogen bromide on germanous bromide,[43,44] it is less stable than the chlorine analogue which it otherwise resembles; it begins to dissociate above 10° while the melting-point lies between −24° and −25°.

Germanous Bromide, $\mathrm{GeBr_2}$.—Colourless plates or needles, m.p. 122°, subliming with some decomposition at 125° and formed by vacuum distillation of the mixture of $\mathrm{GeHBr_3}$ and $\mathrm{GeBr_4}$ arising from the action of hydrogen bromide on the metal at 400°. When the mixture is maintained at 90° *in vacuo* the bromoform decomposes into dibromide and hydrogen bromide and the latter is pumped off together with the tetrabromide. Germanous bromide is also obtained by reducing the above mixture with zinc, filtering off zinc bromide and removing the unaltered tetrabromide as before. The dibromide dissolves in alcohol and acetone the solutions having reducing properties; water hydrolyses it to germanous oxide while bromine and hydrobromic acid produce tetrabromide and bromoform respectively.[43,44] Solutions of germanous bromide in hydrobromic acid give precipitates with cæsium and certain quaternary ammonium and arsonium bromides.[129]

Germanic Bromide, $\mathrm{GeBr_4}$.—Prepared similarly to the tetrachloride although the rereaction between the elements is not as vigorous; colourless, octahedral crystals, m.p. 26·1°, b.p. 186·5°, d^{25}_{25} 3·1315, n^{25}_{D} 1·6269, specific conductivity <0·00008 mho. at 30°; the liquid exhibits to a marked degree the phenomenon of supercooling. In properties it closely resembles its chlorine analogue.[2,16,22,93,159]

Iodogermanes.—Iodomonogermanes, although stated to be formed, have not been isolated.[65]

Germanous Iodide, $\mathrm{GeI_2}$.—When the mixture of chlorides arising from the action of hydrogen chloride on germanium is converted to oxides and treated with hydriodic acid there is formed the sparingly soluble tetraiodide and the more soluble diiodide. On fractional crystallisation from hydriodic acid the diiodide is obtained as yellow hexagonal plates resembling lead iodide; the crystal structure is of the C6 type.[160] It sublimes above 240° with some decomposition, is insoluble in hydrocarbons, slightly soluble in chloroform and readily dissolves in water and dilute acids.[17,43,65] The solution in hydriodic acid gives a black precipitate with solid cæsium chloride.[141]

Germanic Iodide, $\mathrm{GeI_4}$.—Iodine vapour acts on germanium at 360°, forming not only the orange tetraiodide but also some yellow diiodide,[17] the former is therefore best obtained by evaporating a solution of the dioxide in hydriodic acid and crystallising the residue from chloroform or carbon tetrachloride[93]; the crystals are isomorphous with those of stannic iodide.[32,155] The colour of the iodide varies with temperature being canary-yellow at −185° and ruby-red at 140°; m.p. 146°,[17] b.p. 350–400°,[1] with decomposition, d^{26}_{26} 4·3215; it may be sublimed without appreciable decomposition if carefully heated just above the melting-point. Many organic media dissolve it, but the solutions in alcohol, acetone, ether and pyridine decompose immediately; carbon tetrachloride solutions give white precipitates with dry ammonia and many amines.[17,87,109]

Germanium and Oxygen.

Germanous Oxide, GeO.—Formed as a black sublimate by heating the dioxide in carbon monoxide or a mixture of dioxide with carbon or germanium at 850–900° in nitrogen. At these temperatures it attacks quartz and porcelain glaze and the operations must be conducted in unglazed porcelain; the monoxide begins to sublime at about 710°. It is more easily prepared by reducing germanic salt solutions with zinc and sulphuric acid or, better, with hypophosphorous acid, precipitating orange yellow *germanous hydroxide* with ammonia and drying this in nitrogen at 650° when the black crystalline oxide is formed.[55,76] The hydroxide or, more probably, hydrous oxide is also obtained by hydrolysis of the dihalides; it is easily soluble in alkalis and in the halogen acids.[55,130]

The crystalline monoxide is stable in air at ordinary temperatures and is only slowly attacked by acids, alkalis or oxidising agents. With chlorine or bromine at 250° it forms the tetrahalide and dioxide while hydrogen chloride at 175° produces germanochloroform.

For the band spectrum of GeO, *see* Shaw [110] and Sen Gupta.[154, 163]

Germanic Oxide (Germanium Dioxide), GeO_2.—The oxide is usually obtained by one of the following processes: (*a*) heating the finely divided metal in oxygen or with nitric acid [1] or hydrogen peroxide [19]; (*b*) oxidising the sulphide with nitric acid [1, 24, 35] or with hydrogen peroxide and ammonia [29]; (*c*) hydrolysis of the tetrahalides or sulphide. Although no hydroxide is known the product obtained from aqueous solution must be ignited at 900–1,000° to remove all moisture, while the preparation from oxidation of the sulphide tends to retain sulphuric acid from which it may be freed by moistening with ammonia and re-igniting.

Germanic oxide is a heavy white microcrystalline powder and can exist in two or more allotropic modifications. Evaporation of an aqueous solution of the oxide followed by heating to temperatures between 225° and 1,000° (optimum 380°) gives a product partly converted to a form insoluble in water, hydrochloric or hydrofluoric acid and only slowly soluble in hot alkalis.[24] Conversion into this insoluble modification is catalysed by water vapour or by a mixture of lithium and potassium chlorides. Hydrolysis of the tetrachloride or devitrification of the glass produced on fusing the dioxide leads to a soluble variety; the two forms are enantiotropic with a transition temperature at 1,033°. The soluble oxide is unstable below this and has a stable melting-point at 1,116°; its density at 25° is 4·228, refractive index ω 1·695 while the crystal structure is trigonal-trapezohedral and isomorphous with α-quartz.[96] The insoluble modification has an unstable melting-point at 1,086°, d^{25} 6·239, refractive index ω 1·99, crystal structure, tetragonal and isomorphous with rutile.[58, 105]

The solubility of the oxide in sulphuric or hydrochloric acid is small and decreases with the concentration although with the latter a minimum is reached at 3·5*N*. Alkalis readily dissolve it while the solubility in water at 25° is about 4·5 g. per 1,000 g. H_2O.[61, 96] The aqueous solution is partly colloidal and the solubility depends on the ratio of GeO_2 to H_2O in the original oxide.[88] It is weakly acid and contains H_2GeO_3, dissociation constant of which, according to Schwarz and Huf,[88] is $0{\cdot}5 \times 10^{-7}$; Gulezian and Müller [97] give $1{\cdot}3 \times 10^{-9}$ for this constant and 31·3 for the mobility of the $HGeO_3'$ ion while Pugh [61] states that the acid is dibasic the first dissociation constant being $2{\cdot}6 \times 10^{-9}$ and the second $1{\cdot}9 \times 10^{-13}$. When the dioxide is heated to 1,400–1,500° it fuses to a clear glass, d^{25} 3·637, refractive index 1·607. The dispersive power and thermal expansion are greater than for fused silica while the transmission in the ultra-violet is smaller. A number of glasses have also been made corresponding to the various silicate glasses. Fused germania attacks platinum, quartz and glazed porcelain and fusions must be carried out in unglazed porcelain and out of contact with reducing gases or carbonaceous matter. The fused oxide is acted on by water and acids and devitrifies on heating below the fusion point.[39, 57, 133, 157]

A germanium dioxide gel having adsorptive power of the same order as silica gel has been made from germanium ethoxide, $Ge(OEt)_4$, alcohol and water.[92] No definite hydrate of germanium dioxide exists.[89]

Salts of Germanic Acids.—Most of the salts are derived from the *meta acid*, H_2GeO_3, but a number of *orthogermanates* are known while salts of condensed ortho acids such as the germanium analogues of *Thortveitite*, $Sc_2Si_2O_7$, and *Benitoite*, $BaTiSi_3O_9$ (*q.v.*) have been synthesised. The general method of preparing these complex salts is by fusing or sintering intimate mixtures of the oxides in stoichiometric proportions.[84]

Some of the metagermanates, notably the Li (anhydrous), Na (7 and $6H_2O$), Sr (anhydrous) and Ba (4 and $5H_2O$) salts, have been obtained crystalline from aqueous solution. They are decomposed by carbon dioxide and the solutions therefore slowly deposit GeO_2 on exposure to air. From solutions of copper salts, sodium metagermanante precipitates a basic copper salt, $2CuO,GeO_2,H_2O$, while with aluminium chloride there is deposited a germanate,

$$Al_2O_3,2GeO_2,nH_2O,$$

in which the water is zeolitic.[41, 68, 71]

Magnesium orthogermanate is used in the estimation of germanium and is precipitated in amorphous form by treating germanium solutions with magnesium sulphate, ammonium sulphate and ammonia; when crystalline it is isomorphous with *Forsterite*, Mg_2SiO_4.[9, 84]

Hydrogen peroxide at 0° acts on a concentrated solution of sodium metagermanate to precipitate *sodium perdigermanate*,

$$Na_2Ge_2O_7,4H_2O,$$

while from the filtrate alcohol deposits *sodium permetagermanate*, $Na_2GeO_5,4H_2O$. A *potassium perdigermanate* is also known.[70]

Complex Acids of Germanium.—Addition of mannitol, glycerol or other poly-hydroxy alcohols increases the solubility of germanium dioxide in water and the resulting complex acids may be titrated with sodium hydroxide as in the case of boric acid.[56, 149]

Like silicon, germanium forms *heteropoly acids* with molybdic and tungstic acids. These have been given the formulæ $H_8[Ge(Mo_2O_7)_6]28H_2O$ and $H_8[Ge(W_2O_7)_6]28H_2O$, although they should probably be regarded as

$$H_4GeX_{12}O_{40},29H_2O\ (X{=}Mo \text{ or } W);$$

other hydrates are also known.[70, 78, 82, 134, 140] Derivatives of 10-*tungstogermanic acid*,

$$H_7GeW_{10}O_{32},$$

have been made but the acid itself has not been isolated.[82]

Germanium also forms a complex *germano-oxalic acid*, $H_2Ge(C_2O_4)_3$, of which the *quinine* and *strychnine* salts have been prepared.[158]

Germanium and Sulphur.

Germanous Sulphide, GeS.—Two modifications are known, a red amorphous variety and a dark brown or black crystalline form. The former results when hydrogen sulphide is led into neutral or slightly acid solutions of germanous salts[1, 55]; it dissolves in hydrochloric acid, and in aqueous alkali hydroxides and polysulphides while oxidising agents readily attack it. Acidification of the hydroxide and polysulphide solutions leads respectively to the deposition of mono- and disulphide. Amorphous germanous sulphide gives germanochloroform with hydrogen chloride at 150°, is slowly oxidised by air at 350° while in nitrogen at 450° it is transformed into the crystalline variety.[76] The latter is also obtained by heating the disulphide either with germanium in a stream of CO_2 or with hydrogen at 480°. It may be prepared from the dioxide by heating this in a mixture of hydrogen sulphide and hydrogen at 700°, any disulphide formed being removed by digesting the product with dilute ammonia.[1, 45 83] The crystals are orthorhombic and consist of graphite-like tablets showing pleochroism in the thinnest flakes.[106] The sulphide sublimes in nitrogen at 430° and has m.p. 625°,[76] (530°),[83] and d_4^{20} 3·78 (d_{14}^{14} 4·01). It is more stable than the amorphous variety, being only slowly attacked by oxidising agents and being almost insoluble in mineral acids and cold alkalis.

Germanic Sulphide, GeS_2.—Strongly acid solutions of quadrivalent germanium give the colourless disulphide with hydrogen sulphide precipitation being complete when the solutions are 3–4N with respect to HCl or 5–6N to H_2SO_4 and organic acids are absent. The sulphide is appreciably soluble in water and must be washed with acid solutions saturated with hydrogen sulphide; any admixed sulphur is removed by heating in an inert gas.[29]

Crystalline germanic sulphide is obtainable: (*a*) by heating *germanite* in N at 850–900° after removal of S and As,[123] (*b*) by subliming the monosulphide in sulphur vapour, (*c*) by heating GeO_2 in a stream of H_2S and S at 700–800°; with H_2S alone some monosulphide is formed.[88] This variety forms clusters of white needles melting at about 800° to a dark liquid congealing on cooling to a transparent amber mass; it sublimes above the melting-point; density of the crystals at 140° 2·942, and of the congealed mass 5·81.

The amorphous sulphide is slowly hydrolysed by moist air and readily so by boiling water or steam. It dissolves in alkalis and ammonia, such solutions being easily oxidised with hydrogen peroxide. With alkali sulphides it forms *thio salts* and alkali thiogermanates of the type $M_6Ge_2S_7,9H_2O$ have been isolated[70]; esters of tetrathio-orthogermanic acid, $Ge(RS)_4$, have also been made.[119]

Germanic Sulphate, $Ge(SO_4)_2$.—Obtained when $GeCl_4$ and SO_3 (1:6 mol.) are heated in a sealed tube at 160° for 14 hours. After removal of unaltered reactants and $S_2O_5Cl_2$ the residue solidifies to a white mass easily hydrolysed by water and giving sodium germanate and sulphate with sodium hydroxide.[89]

Germanium and Nitrogen.

Germanium Nitrides.—*Germanous nitride*, Ge_3N_2, is stated to be formed as a brown substance by thermal decomposition of germanous imide, $GeNH$, or of *germanic nitride*, Ge_3N_4.[79, 128] The last compound is prepared by passing ammonia over the metal or dioxide at 700° or when *germanam*, Ge_2N_3H, is heated above 300°. These processes give products differing in colour, that from germanam being colourless while the first method generates what is possibly a brown polymer.[79, 69] Both forms are very stable, being attacked by H_2, O_2 or Cl_2 only above 600°.

Germanium Imides.—Germanous iodide reacts quantitatively with gaseous ammonia at − 33·5° to form the bivalent *imide*, $GeNH$, which is decomposed by water or dilute alkalis yielding ammonia and germanous hydroxide; it is violently oxidised by oxygen.[98] *Germanic imide*, $Ge(NH)_2$, is made by treating $GeCl_4$ with liquid ammonia and removing ammonium chloride by repeated washing with liquid ammonia.[69, 91] It is a white amorphous powder, stable at room temperature in the absence of moisture, and loses ammonia above 150°, producing germanam, a substance of similar appearance stable up to 300°.

Germanium and Carbon.

Aliphatic Derivatives of Germanium.—Tetraalkyl compounds of the type, GeR_4, are prepared: (*a*) by the Grignard reaction on the tetrahalides, (*b*) by the action of zinc dialkyls on these halides or (*c*) by heating alkali- or alkaline-earth metal alloys of germanium with alkyl chlorides or bromides under pressure and in the presence of chlorides of Zn, Fe or Al as catalysts (G.P. 428637). They are colourless liquids with pleasant odours, the lower members being inflammable and burning with reddish-yellow flames. They are slightly soluble in water and readily so in many organic solvents; oxidising agents and halogens attack them but slowly.

Germanium Tetramethyl, $Ge(CH_3)_4$.—Prepared by method (*a*) above but cannot be separated from ether by distillation; the solvent may be removed with sulphuric acid; the tetramethyl compound has b.p. 43·4°, m.p. −88°, d_0^0 1·003, $n_D^{23·5}$ 1·3868.[38, 57, 144]

Germanium Tetraethyl, $Ge(Et)_4$.—B.p. 163·5°, m.p. −90°, $d^{24·5}$ 0·991, $n_D^{17·5}$ 1·443.[2, 28, 30, 57, 75, 99]

The n-*propyl*, n-*butyl* and iso-*amyl* derivatives are also known.[30, 50, 57]

Lower Alkylated Compounds.—These have only been obtained in the methyl and ethyl series, the latter being by far the more complete.

Trimethylgermanium Bromide,

$Ge(Me)_3Br$.

Prepared by demethylating $GeMe_4$ with HBr in the presence of aluminium chloride. Colourless liquid, b.p. 113·7°, m.p. −25°, d_4^{18} 1·544, n^{18} 1·4705. It is hydrolysed by water to a volatile liquid, presumably the oxide $(GeMe_3)_2O$, and yields an amine with dry ammonia.[75]

Methyl iodide acts on cæsium germanous chloride, $Cs[GeCl_3]$, producing *methylgermanium trichloride*, $MeGeCl_3$, while methylene iodide gives *germanium methylene hexachloride*, $Cl_3Ge{\cdot}CH_2{\cdot}GeCl_3$, which is hydrolysed by water to *germanomalonic acid*, $CH_2(GeO_2H)_2$.[142]

Triethylgermanium Bromide, Et_3GeBr.—Results from the action of bromine in ethyl bromide on $GeEt_4$; colourless mobile liquid, b.p. 190·9°, m.p. −33°, it is hydrolysed by dilute alkalis to the *oxide*, $(GeEt_3)_2O$, which boils at 253·9° and from which the other halides may be obtained.[99] With sodium sulphide the halides yield *triethylgermanium sulphide*, $S(GeEt_3)_2$,[147] while with sodium under pressure or lithium in ethylamine they give *hexaethyldigermane*, $[Et_3Ge]_2$, b.p. 265°/758 mm. The latter is decomposed by lithium (or potassium) in ethylamine, forming *lithium* (*potassium*) *triethyl germanide* which generates the tetra-ethyl derivative with ethyl bromide and reacts with ammonia, producing *triethylgermane*, $GeHEt_3$, a colourless liquid with camphor-like odour, b.p. 124·4°/751 mm.; it decolourises bromine in ethyl bromide and evolves hydrogen with potassium amide.[99]

Triethylgermanium fluoride reacts with bromine in ethyl bromide giving a product converted by sodium hydroxide into *diethylgermanium oxide*, $GeEt_2O$.[100] This oxide exists in two forms, a colourless amorphous powder, m.p. 175°, and an unstable liquid which is slowly transformed into the solid; the transition temperature is about 110°. Hydrobromic acid converts the oxide into *diethylgermanium dibromide*, $GeEt_2Br_2$, b.p. 202° from which *diethylgermaniumimine*, $GeEt_2NH$, is formed with liquid ammonia. The dibromide is also obtained by treating diphenyldiethylgermane with bromine.[100]

$$GePh_2Et_2 + 2Br_2 = GeEt_2Br_2 + 2PhBr.$$

Ethylgermanium triiodide, $GeEtI_3$, is produced when germanous iodide and ethyl iodide are heated at 160° for 3 days in the absence of air; lemon-yellow liquid, b.p. 281°/755 mm., m.p. $\sim -2°$; soluble in organic solvents, partly hydrolysed by water. The aqueous solution with freshly prepared silver oxide forms *ethylgermanic oxide*, $(EtGeO)_2O$, a glass-like solid not melting at 300° and from which the other halides are obtained. The oxide is better prepared by ammonolysis of the iodide followed by hydrolysis. The white intermediate product gives the *nitride*, $GeEtN$, on heating in a closed tube to 150°.[117]

Heating ethylgermanium triiodide with a lead bismuth alloy at 150° in the absence of air yields a product, probably $(GeEtI)_x$, which with ethyl halides at 125° forms the diethylgermanium dihalides.[118]

AROMATIC DERIVATIVES OF GERMANIUM.—These are now so numerous that it is not possible to do more than indicate the types of compounds obtained and the general methods of preparation as exemplified in the phenyl series.

Germanium Tetraphenyl, $GePh_4$.—Obtained by the action of $GeCl_4$ or $GeBr_4$ on (*a*) a large excess of phenyl magnesium bromide (36 mol.), (*b*) the product from the interaction of phenyl magnesium bromide and zinc chloride and (*c*) bromobenzene and sodium. White crystalline solid, m.p. 235·7°, insoluble in water and unaffected by boiling aqueous alkalis or cold concentrated H_2SO_4; sparingly soluble in alcohol, ether and petrol, easily so in hot benzene, toluene or chloroform.[30, 31, 49, 57, 136]

Sodium Triphenylgermanide, $NaGePh_3$.—Formed when sodium in liquid ammonia acts on hexaphenyldigermane or germanium tetraphenyl and crystallising from liquid ammonia with 3 mol. NH_3 which are readily lost. The germanide is very reactive, easily oxidised to the *germanolate*, Ph_3GeONa, yields tetra-aryl or triarylalkyl derivatives with aryl or alkyl halides.[49, 80, 95]

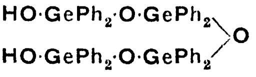
Triphenylgermane, Ph_3GeH.—Generated when the above germanide is treated with water or ammonium bromide; it exists in two forms, one melting at 47° and the other at 27°, the former being the stable modification at room temperature. It is slowly oxidised in air, reacts with halogens or halogen acids forming triphenylgermanium halides, while with sodium in liquid ammonia, $NaGePh_3$, is obtained.[49]

Triphenylgermanium Halides, Ph_3GeX.—The bromide is prepared by acting on germanium tetraphenyl in chloroform or ethylene dibromide with hydrogen bromide or bromine. It is also the chief product of the Grignard reaction when only 5 mol. of $PhMgBr$ are used per mol. of $GeBr_4$. Hydrolysis leads to the *oxide*, $(Ph_3Ge)_2O$, colourless prisms, m.p. 182–183°, from which the other halides may be obtained. These are colourless crystalline solids soluble in the usual organic media and fairly readily hydrolysed; the melting-points are: *fluoride* 76·6°, *chloride* 117–118°, *bromide* 138·7° (134°), *iodide* 157°. With KNH_2 in liquid ammonia the bromide yields Ph_3GeNHK and this with ammonium bromide forms the *amine*, Ph_3GeNH_2, which readily loses ammonia, giving a mixture of the secondary amine, $(Ph_3Ge)_2NH$, and the tertiary amine, $(Ph_3Ge)_3N$; the latter is better obtained by heating the primary amine at 200° *in vacuo*.[31, 49, 50, 57, 80, 81]

Triphenylgermanol, Ph_3GeOH.—Prepared from sodium triphenylgermanolate by treating its benzene solution with water and evaporating. The colourless crystals contain benzene and are recrystallised from light petroleum; it melts at 134·2° and is slowly converted to the oxide on heating.[30, 49, 80]

Diphenylgermanium Compounds.[31, 81, 90]—*Diphenylgermanium dibromide*, Ph_2GeBr_2, is obtained by heating $GePh_4$ for 10 hours with bromine in carbon tetrachloride. The resulting mixture of bromides is converted through the oxides into the chlorides which are more readily fractionated; the fraction distilling at 100°/0·005 mm. contains pure *diphenylgermanium dichloride*. The halides are colourless liquids soluble in organic solvents and slowly hydrolysed by moist air; the *fluoride* and *bromide* distil at 100° and 120° respectively at 0·007 mm. The latter is also formed when $GePh_4$ and $GeBr_4$ are heated together at 210–290° and as a by-product in the preparation of Ph_3GeBr by the Grignard reaction.

The oxide obtained by hydrolysing the halides is not a single substance and Morgan and Drew have isolated from it *trianhydrotetrakisdiphenylgermanediol,*



and the closed-ring *tetraanhydro* derivative.

Monophenyl Derivatives.[31, 81, 90, 120, 142]—*Phenylgermanium trichloride,* $PhGeCl_3$, is prepared (*a*) by heating $GeCl_4$ and $GePh_4$ under pressure, (*b*) by heating $GeCl_4$ and mercury diphenyl at 140° in xylene and (*c*) by heating iodobenzene with $Cs[GeCl_3]$ at 250°. It is a colourless liquid, b.p. 105–106°/12 mm.; the *tribromide* boils at 120–122°/13 mm. while the *triiodide* is a solid, m.p. 55–56°. Hydrolysis of these leads either to *phenylgermanonic acid,* $PhGeOOH$, or its anhydride.

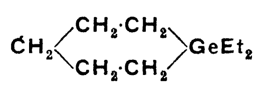
POLYGERMANIUM PHENYLS.

Hexaphenyldigermane, $Ph_3Ge—GePh_3$.—Formed during the prolonged action of $PhMgBr$ on $GeCl_4$ or by the electrolysis of Ph_3GeNa in liquid ammonia, it is usually obtained by heating Ph_3GeBr with sodium in xylene or by the interaction of Ph_3GeNa and Ph_3GeF. Colourless microcrystalline powder, m.p. 340°, only slightly soluble in organic solvents.[31, 49, 136, 137]

Octaphenylgermanopropane, Ph_8Ge_3.—Prepared by the action of 2 mol. of Ph_3GeNa on 1 mol. of Ph_2GeCl_2 in warm benzene; it forms colourless plates from chloroform, m.p. 247–248°, and is stable towards moisture.[81]

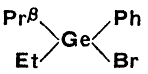
Sodium in xylene reacts with diphenylgermanium dichloride to yield some *germanium diphenyl,*[81] probably $(Ph_2Ge)_4$, a white crystalline material, m.p. 294–295°. The corresponding reaction with the trichloride, $PhGeCl_3$, gives a *product,* $(GePh)_6$, which was first thought to have a cyclic structure but which is now regarded as an open-chain compound.[90, 146]

The only definite ring structures containing germanium appear to be 1:1-*diethylgermaniumcyclopentamethylene*



and the corresponding 1:1-*dichloro* derivative. The latter is made from the Grignard reagent of α:ε-dibromopentane.[108]

ARYL-ALKYL DERIVATIVES OF GERMANIUM.—A number of mixed aryl-alkyl germanium compounds have been made of which the most interesting is probably *ethylisopropylphenylgermanium bromide*

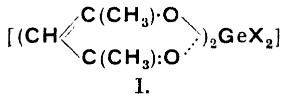


on an analogy with carbon the germanium atom is asymmetric but the compound has not been resolved.[90]

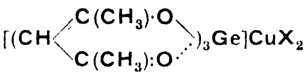
Germanium Derivatives of β-diketones.[22]—Germanium tetrachloride reacts with acetylacetone in anhydrous solvents, forming *germanium bisacetylacetone dichloride* (I), colourless prisms, m.p. 240°, sparingly soluble in organic media. With the tetrabromide the reaction is slow and the yield is poor; the *dibromide* is a colourless microcrystalline powder, m.p. 226°. The corresponding propionylacetone derivatives have also been obtained.

With copper acetylacetone germanic chloride gives unstable complex intermediate products which resolve on crystallisation into *germanium trisacetylacetone cuprochloride* (II), colourless refractive prisms, m.p. 147–148°. The analogous *cuprobromide* is obtained in a like manner but is accompanied by a dicuprobromide,

$$[Ge(C_5H_7O_2)_3]Cu_2Br_3.$$



I.



II.

X = Cl or Br

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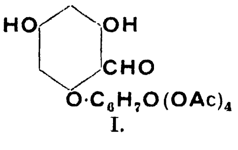
G. R. D.

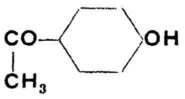
GERSDORFFITE. Sulpharsenide of nickel, **NiAsS**, crystallised in the cubic system. The nickel (35·4% according to the formula) is usually partly replaced isomorphously by iron, and less often by cobalt. Analyses show **Ni** 16·24–35·97%, with **Fe** nil–16·64 and **Co** nil–14·12%. Crystals are usually octahedral in habit, and they show good cleavages parallel to the faces of the cube. The colour is steel-grey with metallic lustre, but usually the material is tarnished and dull black; the streak is greyish-black. Sp.gr. 5·6–6·2; hardness 5. The mineral occurs in metalliferous veins, and has been recorded from several localities in central Europe; also from Loch Fyne in Scotland, Sudbury and Cobalt in Ontario, etc.

L. J. S.

GESNERIN. The flower petals of *Gesnera fulgens* contain an anthocyanin which is unique in that it is directly related to the flavones rather than to the flavonols. It has been studied by G. M. and R. Robinson and Todd (J.C.S. 1934, 809) who, although unable to isolate the anthocyanin because of lack of flowers, have shown that gesnerin is 5-glucosidylapigeninidin (III). The pigment was extracted from the petals by means of hot 0·2% **HCl**, after rejecting the darker bluer-red portions. A long and tedious purification afforded a solution of the anthocyanin, which showed properties identical with those of a synthetic preparation. 2-O-Tetra-acetyl-β-glucosidylphloroglucinaldehyde (I) condensed with 4-hydroxyacetophenone (II) by means of **HCl** in dry ethyl acetate afforded an acylated anthocyanin, from which (III) was obtained by treatment first with **NaOH** and then with **HCl**.



I.



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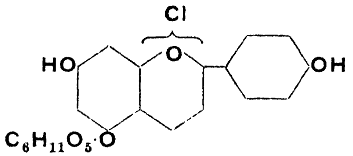

III.

The *chloride* was obtained in the form of small brownish needles of the *tetrahydrate*,

$$C_{21}H_{21}O_9Cl,4H_2O,$$

when a solution in hot 0·1% HCl was mixed with an equal volume of 5% methyl-alcoholic HCl. A *basic chloride*, $2C_{21}H_{20}O_9,HCl,8H_2O$, when dried in air, and $2C_{21}H_{20}O_9,HCl,H_2O$, after drying at 110° in a high vacuum over phosphorus pentoxide, separated in the form of minute brown crystals when the acid concentration of a 0·1% HCl solution was increased to 2%. The *chloride* is almost insoluble in 2% HCl or in acetic acid; it dissolves sparingly in 0·5% HCl to a yellowish-brown solution. The orange-yellow alcoholic and *n*-butyl-alcoholic solutions exhibit a green fluorescence. The aqueous or alcoholic solution gives a fine bluish-rose coloration on the addition of sodium acetate, sodium carbonate, ammonia or sodium hydroxide. The distribution to *iso*amyl alcohol is superficially similar to that of a normal diglucoside. Under the conditions defined by Robinson and Todd (J.C.S. 1932, 2296, 2492), the distribution number (*n*-butyl alcohol) is 50 (3·18 mg. in 50 c.c. of the mixed solvents).

W. B.

GETAH WAX *v.* Fig Tree Wax.

GEYSERITE or SILICEOUS SINTER. (Ger. *Kieselsinter.*) An opaline form of hydrated silica deposited by the hot springs (geysers) of volcanic regions. It is white or greyish in colour and porous in texture. On the exterior it usually assumed fantastic shapes—stalactitic, filiform and cauliflower-like masses—and it is sometimes found encrusting plants. Compact-massive and pulverulent forms also occur. Sp.gr. 1·8–2·0. The material consists of nearly pure silica, SiO_2 82–97% with H_2O 3–10%, and small amounts of aluminium, iron, calcium, magnesium and alkalis. Immense deposits occur in Iceland, New Zealand, Luzon in the Philippine Islands, Azores, and Yellowstone National Park in Wyoming. Its use has been suggested for the manufacture of porcelain, glass, silica-glass, etc., and as an inert filling material.

L. J. S.

GHEDDA or East Indian (Bees') Wax. The wax secreted by the oriental species of bee, *Apis indica* Fab., *A. florea* Fab., and *A. dorsata* Fab. M.p. 62–63°, solidifies at 59–58°, acid value 5–7·5 ester value 86·92.

GHEE (Hindustani, "*Ghi*") consists of clarified butter fat and is extensively employed in India as a general edible and cooking fat; it also finds considerable use as an external medicament (very old ghee is regarded with especial favour for this purpose) and in religious ceremonies. It is prepared by heating ("boiling") butter until most of the water has evaporated and the fat layer becomes clear and can be separated from the curd and residual water by decantation and/or straining. The quality and flavour of the preparation, which naturally depends upon the care exercised in the manufacture of the butter (*v.* Butter) and in its subsequent treatment, is gradually improving, as modern procedures replace the older crude native methods (Kothavala and Cox, J. Central Bur. Animal Husbandry Dairying, India, 1927–28, **1**, 95; French, Bull. Imp. Inst. 1936, **34**, 32). The best quality of ghee is a white or yellow fat of fresh butter-like flavour, which keeps indefinitely if stored in porous earthenware vessels, whilst the lower grades, which have been imperfectly clarified in the primitive native processes, soon develop a characteristic flavour and sharp rancid taste. Ghee of good quality may also be manufactured directly by boiling (clarifying) washed fresh cream, or soured cream (French, *l.c.*; Bull. Imp. Inst. 1938, **36**, 349; Dave, Poona Agr. Coll. Mag. 1935, **26**, 142).

The purified dry butterfat has better keeping properties than ordinary butter and, hence, ghee-like preparations made from local butters are to be found not only in other hot countries such as Egypt (where the fat is termed "Samna"), Nigeria and Tanganyika, but among peasant populations in Russia, Germany (as "Schmelzbutter" or "Butterschmalz"), etc.

In India, the fat sold under the name of "ghee" may be derived from cow butter or buffalo butter or from mixtures of both, and ordinarily no distinction is made between the two varieties, even in the matter of price. Ghees prepared from the milk of other animals, such as goats, may also be met with in some countries.

The following figures are reported by Godbole and Sadgopal from the examination of a number of authentic Indian butterfats ("Butterfat (Ghee)," Benares, 1939, p. 17; *cf.* Bhattacharya and Hilditch, Analyst, 1931, **56**, 161):

TABLE I.—PROPERTIES OF INDIAN BUTTERFATS (GODBOLE AND SADGOPAL).

	Cow butterfat.	Buffalo butterfat.
Specific gravity at 15°C.	0·9358–0·9443	0·9340–0·9444
Refractive index (butyro-refractometer at 40°)	40·0–43·0°	40·0–43·5°
Melting-point . . .	28·5–42·0°C.	32·0–43·5°C.
Saponification value .	225·5–236·0	228·5–236·0
Reichert-Meissl value .	21·0–34·4	24·6–35·5
Polenske value . .	0·7–1·95	0·8–2·2
Bertram A-value . .	6·2–7·0	6·3–7·4
Bertram B-value . .	31·0–35·5	32·9–35·5
Iodine value[1] . . .	31·5–45	26·5–44·0
Thiocyanogen value[1] .	25·5–40·8	22·7–40·0

[1] *Cf.* Budhalakoti and Mukherji, J. Indian Chem. Soc. 1935, **12**, 455; iodine values 30–50.

The Kirschner values of cow-butter ghee and buffalo-butter ghee (two samples each) examined by Bhattacharya and Hilditch (*l.c.*) were 20·6–20·9 and 24·6–25·6 respectively.

It will be noted that the figures for both fats fall within the ranges of values commonly accepted for European butterfats (*v.* BUTTER). The butyric acid values of six samples of standard butters from the Indian market examined by Godbole and Sadgopal (*op. cit.* p. 77), however, range from 24·1–26·0 (average 25·2), which is considerably higher than the average figure of 20 reported by Grossfeld for European butter fats. Correspondingly, the content of butyric and caproic acids in the Indian fat appears to be slightly higher than that of the European butter fats (Sadgopal). Bhattacharya and Hilditch (*l.c.*) give the following figures for the percentage composition of the fatty acids from two samples [1] of first quality buffalo ghee having iodine values respectively 32·5 and 33·5 : butyric acid 3·9, 4·1 ; caproic acid 1·7, 1·4; caprylic acid 0·3, 0·9; capric acid 0·9, 1·7; lauric acid 2·0, 2·8; myristic acid 7·2, 10·1; palmitic acid 20·0,[1] 31·1; stearic acid 24·4[1], 11·2; arachidic acid 2·7, 0·9; oleic acid 34·3, 33·2; linolic acid 2·6, 2·6. Figures approximating to those for the second sample have been reported by Godbole and Sadgopal (*op. cit.* p. 18) as the average results of the examination of more than forty samples of buffalo ghee. These analyses show that the proportion of butyric and stearic acids in buffalo-butter fat is distinctly greater than in cow-butter fat, and the proportion of linolic to oleic acid is lower; arachidic acid has also been detected in the acids of buffalo-butter fat, but is absent from cow-butter fat (Bhattacharya and Hilditch).

The glycerides of the second sample of buffalo ghee described above were found to comprise about 34 mol.-% of fully saturated triglycerides and 42–54 mol.-% of mono-unsaturated-di-saturated glycerides, the balance consisting of di-unsaturated and/or tri-unsaturated glycerides. Allowing for its particular content of linolic and oleic acids, the general structure of the fat is thus comparable to that of cow-butter fat (*v.* BUTTER), and, as in the case of other animal fats, is of the "mixed heterogeneous" type: *i.e.* there is no evidence of any selective association of unsaturated and saturated acids, or of segregation of any particular fatty acid in the form of simple triglyceride.

Standards for ghee, which have been laid down by the Ghee Conference of the Government of India, 1937–38 (Schedule III: normal physical and chemical constants of "Ghee" to which designation marks may be applied) are shown in Table II; these standards are severely criticised by Godbole and Sadgopal on the ground that the limits given for various characteristics are too narrow and liable to exclude a very large number of genuine samples of cow and buffalo ghee (*cf.* Brahmachari, Indian Med. Gaz. 1935, **70**, 71).

TABLE II.

	Cow ghee, yellow label.	Buffalo ghee, blue label.	Special, red label.	General, green label.
Butyro-refractometer at 40°C. . . .	40·5–42·5°	40·5–42·5°	40·5–42·5°	40·5–43·5°
Moisture	≯0·5%	≯0·5%	≯0·5%	≯0·75%
Saponification value	222–226	226–234	222–234	220–236
Reichert-Meissl value	26–28	≮30	≮28	≮24
Polenske value	1·5–2·5	1·0–1·75	1·0–2·0	0·5–2·5
Kirschner value	20–25	≮25	—	—
Free fatty acids as oleic acid . . .	≯1·5	≯1·5	≯1·5	≯2

Concerning the content of vitamin-A in ghee, *see* papers by B. N. Banerjee *et. al.*, in Agric. Live-Stock India, 1935 onwards; Grewal, Quart. J. Pharm. 1933, **6**, 650.

Ghee is liable to be adulterated with animal or vegetable fats or hydrogenated fats of suitable consistency: its analysis follows the lines described for butter fat in the article BUTTER (*see also* "Standard Methods of Analysis for Testing and Grading Ghee," 1938, published by the Government of India; Venkatachalam, Analyst, 1937, **62**, 732; Daroga and Sidheva, Ind. and News, Ed., J. Indian Chem. Soc. 1938, **1**, 91). Godbole and Sadgopal recommend a determination of the dispersion in conjunction with the refractive index as a rapid qualitative sorting test (*cf.* Athavale and Jatkar, J. Indian Inst. Sci. 1938, **A21**, 15); when observations of refractive index are made with a butyro-refractometer in daylight (or arc-lamp light) the appearance of the colour-fringes at the edge of the shadow may afford preliminary indication of adulteration; pure ghee is stated to show a colourless or violet-edged demarcation line, whilst blue or orange fringes are to be observed if animal or vegetable oils and fats are present.

"*Vegetable ghee*" ("vanashpati"), which is sold as a substitute for ghee, bears the same relation to it as margarine does to butter in Europe, and consists of suitable blends of hydrogenated vegetable oils (commonly arachis and cottonseed oils), and vegetable oils and fats.

E. L.

GIALLOLÌNO. Giallo di Napoli, Naples Yellow, a yellow pigment obtained by heating tartar emetic with common salt and lead nitrate and approximating in composition to basic lead antimonate. It has been used for many centuries in enamels and pottery ware, but its use as a paint is now obsolete.

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[1] The first sample was prepared from the milk of of Murrah buffaloes fed on dry grass and green millet with the addition of concentrates containing cotton-seed, sesamé-cake and lentil-husks; the second was a market sample derived from pasture-fed animals. The authors remark in regard to the first sample, that insufficient material was available to permit them to repeat the analysis as they would have wished to do in view of the unexpected results obtained for the contents of stearic and palmitic acids. The presence of arachidic acid, however, is regarded as definitely proved.

GIBB'S CELL (*v.* Vol. III, 53*a*).

GIBBSITE or HYDRARGILLITE. Hydrated alumina, $Al_2O_3 \cdot 3H_2O$ (Al_2O_3 65·4%), crystallised in the monoclinic system. It usually forms white or greyish, stalactitic or mamillated, encrusting masses. Crystals, to which the name *hydrargillite* is more particularly applied, have the form of thin six-sided plates with a pearly lustre on the perfect basal cleavage; these are found in a magnetite-bearing schist at Shishimsk, near Zlatoust in the Urals, and in nepheline-syenite in the Langesund-fjord, Norway. Sp.gr. 2·3–2·4; H. 2½–3½. A bed, about a foot in thickness, of nodular plates of amorphous material is found beneath the soil overlying igneous rocks over a wide area in the Palni Hills in Madras. As a constituent of bauxite and laterite it is of wide distribution, and it has also been identified in some highly aluminous fireclays. If found in sufficient quantity it would be of value as an aluminium ore.

L. J. S.

GILSONITE. A mineral hydrocarbon occurring in Utah, the Philippines and elsewhere. Used in the paving industry and in the manufacture of electrical insulators, roofing materials, for water-proofing pipes, preventing corrosion of iron plates in ships, coating wire fencing, sea walls, etc., for lining tanks for chemicals, in lubricants for heavy machinery, in rubber substitutes and as a binder for briquettes.

Distilled up to 450° it yields 12·75% fuel gas (containing mainly CH_4 carrying 2% light oil and 0·25% NH_3), 55% oil and 30% coke (containing 5–6% N). The oil fractionated in CO_2 gives light solvent oil, intermediate gas oil and a heavy oil yielding lubricating oil and wax. All these oils have both asphaltic and paraffinoid characteristics. The middle fraction purified by H_2SO_4 and sulphonated with oleum gives a clear oil with properties of a refined petrol. The acid sludge yields a semi-drying oil and a solution of sulphonic acids used for hydrolysing fats and the Na salts of which are useful as detergents. The semi-drying oil mixed with linseed oil causes homogeneous drying (U.S.P. 1459328, 1524859, 1573764–5, 1578235).

Gilsonite is rendered completely soluble in petroleum by heating for ½ hour at 160–200° (U.S.P. 1803637).

GIN or GENEVA is a spirituous liquor the characteristic flavour of which is due to the presence of oil expressed from the juniper berry. The term "Gin" is an English abbreviation of "Geneva," a corruption of the French "Genièvre" or the Dutch "Jenever," both of which have reference to the essential flavouring ingredient. There are two main types—the British "Gin," and the Dutch "Geneva," "Hollands" or "Schnapps." The spirit is usually derived from grain—a mixture of maize, malt and rye. For low grade varieties, spirit derived from molasses or other fermentable substances is sometimes used. Whilst there is no legal or official standard for gin, and such substitution may not be detrimental to public health, a case can possibly be established against the marketing of such a preparation as genuine gin.

The English variety is usually prepared from a grain mixture consisting approximately of 15 parts of maize, 3 of malt and 2 of rye. After fermentation, the spirit is generally rectified in patent stills, and although a high alcoholic strength is attained, the rectification is not carried out to such an extent as to eliminate the characteristic flavour of grain spirit. The artificial flavourings in addition to the juniper which are added, are angelica, almond, calamus root, cardamon seeds, cassia buds, coriander seeds, liquorice powder, orris root, sweet fennel and turpentine. The method of adding the flavouring substances varies. In some cases they are added directly, or an alcoholic mash of the flavourings is distilled, the distillate being added to the spirit to be flavoured. Another and probably the best method is to redistil the spirit after the addition of the flavouring ingredients in a kind of pot-still with a longhead or other simple rectifying apparatus.

Sweetened gin, popularly known as "Old Tom" is made by the addition of sugar syrup to plain gin. The syrup is prepared by dissolving refined sugar in its own weight of water. Sometimes the syrup is flavoured with orange flower water and is known as "capillaire." The clear solution is added in the proportion of about 6 gallons of syrup to 100 gallons of gin.

Plymouth gin is a special variety made in Plymouth and consumed extensively in the West of England. It has a characteristic flavour, said to be due to ether resulting from the addition of a little sulphuric acid to the spirit before rectification.

The Dutch variety is usually prepared from equal parts of the three grains above mentioned although sometimes maize is omitted. The manufacture is carried on mainly at Schiedam where pot stills are chiefly employed. The spirit is subjected to three or four rectifications, when it is known as "moutwyn" or "maltwine." This is sold to the manufacturers of Geneva or Hollands who flavour it by methods similar to those above described for English gin. The best Hollands is said to be prepared as follows: A mixture of 2 measures of ground rye with 1 measure of ground barley malt is mashed with about 24 gallons of water for each hundredweight of the mixed meal. The mashing being completed, the specific gravity of the wort is reduced to between 1,033 and 1,038 by the addition of cold water. The mash is then fermented after which the whole is transferred to a still. To the first product of distillation, called "low wines," a varying proportion of juniper berries with a little salt is added, and it is redistilled. To the distillate further flavouring derived from the juniper as well as from the rye or barley used in brewing are added.

The consumption of gin has increased greatly in recent years owing to the establishment in popular favour of apéritifs and cocktails of which it forms the basis. In these preparations the gin is mixed with a variety of different materials such as vermouth, angostura bitters, or citrous extracts. Before this development, however, gin was in much demand on account of its supposedly valuable medicinal properties, particularly in affections of the urinary organs. In this connection the work of Cafferata (v. Ducceschi, Pavia, Arch. ital. biol. 1920, **70**, 93) is of interest. By injection into the jugular vein of the rabbit he established the toxic coefficient (expressed in terms of cubic centimetres per kilogram of body weight) to be 18–20 compared with whisky 10, cognac 13–18, wines 65–80 and beers 152–200.

The adulteration of gin, except by dilution with water, is not common. The Food and Drugs Act, 1938, prescribes that, in proceedings for dilution of gin, it shall be a defence for the defendant to prove that the spirit had been diluted with water only, and that its strength was still not lower than 35° under proof. This provision, however, does not affect Sect. 14 of the Finance Act, 1935, according to which " if any spirits delivered in bottle from a warehouse for home consumption are sold by a dealer in or retailer of spirits at a strength lower than that by reference to which the customs duty or the excise duty chargeable thereon was computed, he shall . . . be liable . . . to a fine." Alkaline carbonates and sometimes alum and salts of zinc and lead have been found. Juniper wood oil and turpentine oil are occasionally used as substitutes for or admixed with the oil from the juniper berry. Dorchies (Ann. Falsif. 1935, **28**, 452), in the examination of a large number of samples from various origins, found considerable variation in the products from different distilleries. He found that constituents other than ethyl alcohol never fell below 352 mg. per 100 ml. of absolute alcohol. The most important of these—the higher alcohols—were never below 270, furfural was present in traces too small to determine except in the product of one distillery which contained 1·0–9·6 mg. per 100 ml. of absolute alcohol.

F. G. H. T.

GINGELLY or **GINGILI OIL**. Syn. for sesamé oil.

GINGER. The dried rhizome, either whole or powdered, of *Zingiber officinale* Roscoe, a plant 3–4 ft. in height, which grows wild in India and China and is cultivated extensively in most tropical countries. At the present time the chief kinds, which find their way into the English market, are Jamaica, Calicut, African, Japanese and, in less quantity, Bombay. As ginger is invariably cultivated from cuttings of the rhizome, it is very seldom that the seed is fertile, and consequently there is little variation in botanical characters wherever the plant is grown. It may be propagated readily in any tropical or sub-tropical climate having a high rainfall. It was at one time stated that Chinese ginger used for preserving purposes was derived from a related plant, *Alpinia galanga*, Fam. Zingiberaceæ, but this is now thought to be erroneous. Japanese ginger is not derived from *Z. officinale*, but is stated to be obtained from *Z. mioga*, and is therefore not employed for medicinal purposes. Ginger has been grown extensively in Nigeria, and a detailed account of its cultivation is given in the Bull. Imp. Inst. 1926, **24**, 667.

The rhizomes are dug up when the plant is about a year old, washed and dried in the sun. In some cases the root is dried intact and in others the epidermis is removed by scraping or cutting. Great care is necessary in the peeling of ginger, as the aromatic principles are found in the cells immediately beneath the epidermis, and if these are spoilt or accidentally removed the spice becomes valueless. Recent reports from Nigeria indicate that the native grower, in his attempt to obtain a good colour, has prolonged unduly the soaking and washing of the ginger with the consequent leaching-out of an unnecessarily large amount of the water-soluble constituents (Bray, Major and Hill, Analyst, 1939, **64**, 176). Active steps are being taken to rectify the faulty curing and these are meeting with considerable success.

Although the official ginger is unbleached, except for the action of the sun, there is a popular prejudice in favour of a white product and to meet this demand various methods of treating the roots are adopted. They are sometimes bleached by means of chlorine or sulphurous acid, or are dusted with calcium carbonate or sulphate, but the commonest method consists in immersing the rhizome in milk of lime. This also prevents the attack of insects. When treatment is carried out after importation, the bleached " hands " are dried off in a moderately hot oven, as sun drying is no longer possible.

The unscraped root has a yellowish-brown wrinkled surface, whilst the scraped variety is smooth and nearly white. The pieces are, as a rule, from 3 to 6 in. in length, knotted and bent, flattened in section and with a short fracture. On being cut with a knife the best ginger presents a soft floury surface, inferior qualities appear hard, resinous and shiny. Ginger is used as a condiment and flavouring agent and in medicine as an aromatic stimulant and carminative.

Microscopic Appearance.—The starch grains associated with the parenchymatous tissue are very abundant and characteristic, they are simple and ovoid in shape, from 7 to 40μ long and 5 to 25μ broad, with an eccentric hilum, and striations are visible in the larger grains, provided that the illumination is properly adjusted. In Japanese ginger the starch grains occur in aggregates and are less eccentric than in other grains.

Scraped ginger contains no cork, but the natural rhizome possesses an outer cork rind of about 0·4 mm. thickness and containing about 20 layers of large yellow or brownish, somewhat flattened, thin-walled cells, without any contents. Immediately beneath is the parenchyma of the cortex containing starch and interspersed with oil cells, whilst further inwards the parenchyma cells are larger and contain more starch grains but fewer oil cells.

The spiral vessels are broad, reticulated and scalariform. The bast fibres are also broad and have rather thin walls.

Chemical Composition.—The chief characteristic constituents are a volatile oil to which the aroma is due; a fixed oil, gingerol, which gives the pungent flavour; starch and resin. The following figures (Richardson, from Leach, "Food Inspection and Analysis," p. 463, 4th ed. 1920, J. Wiley & Sons, New York,) will afford some idea of the composition of whole ginger root.

TABLE I.

	Water.	Ash.	Volatile oil.	Fixed oil and resin.	Starch.	Crude fibre.	Albuminoids.	Undetermined.	Nitrogen.
Calcutta	9·60	7·02	2·27	4·58	49·3	7·45	6·30	13·4	1·01
Cochin	9·41	3·39	1·84	4·07	53·3	2·05	7·00	18·9	1·12
Unbleached Jamaica . .	10·49	3·44	2·03	2·29	50·6	4·74	10·85	15·6	1·74
Bleached Jamaica (London)	11·00	4·54	1·89	3·04	49·3	1·70	9·28	19·2	1·48
Bleached Jamaica (America)	10·11	5·58	2·54	2·69	50·7	7·65	9·10	11·7	1·46

J. F. Liverseege, H. H. Bagnall and A. R. Lerrigo (Yearbook of Pharmacy, p. 467, 1926) record detailed analyses of 24 samples of ground ginger, and the average figures taken from 159 to 338 samples obtained under the Sale of Food and Drugs Acts.

TABLE II.

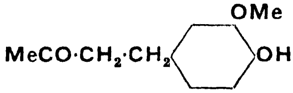
	Maximum.	Minimum.	Average.
Moisture . . .	10·9	9·0	10·1
Ash	6·60	3·14	5·26
Ash soluble in water . . .	2·89	2·0	2·52
Ash insoluble in water, soluble in HCl . . .	3·21	0·74	2·16
Ash insoluble in HCl . . .	1·02	0·04	0·58
Organic matter .	87·1	82·8	83·7
Organic matter ×1·19 . . .	103·6	98·5	99·7
Acetic acid insoluble	80·4	76·0	—
Water extract .	18·2	11·8	12·8
Methylated spirit extract (1·4 g. in 70 c.c.) . . .	7·1	4·3	5·9
90% alcohol extract . . .	7·3	5·0	6·4

Essential Oil (*v.* GINGER, ESSENTIAL OIL OF).—This is best determined by the method of Cocking and Middleton (*v.* this Vol. p. 8*a*).

Fixed Oil.—Determinations by Garnett and Grier (Pharm. J. 1909, **83**, 159–160) give the gingerol as from 1·1 to 2·2%.

The composition of gingerol has been investigated by Lapworth, Pearson and Royle (J.C.S. 1917, **111**, 777), who found the pungent principles of ginger to be a mixture of saturated phenolic compounds derived from a residue of *zingerone* (*v. infra*) in association with a molecular proportion of the residues of saturated aliphatic aldehydes.

Zingerone.—Nomura (*ibid.* 1917, **111**, 769; Sci. Rep. Tôhoku, 1925, **14**, 143) has prepared from ginger, also Lapworth and Wykes from gingerol (J.C.S. 1917, **111**, 790), a ketonic body, zingerone, the yield amounting to about 0·04% of the ginger, to which both publications agree in assigning the formula $C_{11}H_{14}O_3$, the constitution of the ketone being



Zingerone may be obtained in 76% yield by the reduction of 4-hydroxy-3-methoxy-styryl methyl ketone by sodium amalgam in aqueous solution. It forms colourless needles, rhombohedra, or lustrous plates, m.p. 40–41°

TABLE III.—SHOWING RESULTS OF ANALYSIS OF ADULTERATED GINGERS.

	Total ash.	Ash soluble in water.	Ash insoluble in HCl.	Alcohol (90%) extract.	Cold-water extract, %.
Exhausted ginger from English ginger-ale works [1]	2·12	0·59	0·18	4·88	6·15
Exhausted ginger from extract works [1]	5·05	3·55	1·50	1·52	16·42
Exhausted ginger [2]	3·00	1·80	0·34	5·5	6·6
Exhausted ginger [2]	2·68	1·52	0·28	5·0	7·1
Added chalk and sand [2] . . .	15·74	2·20	1·38	5·9	12·6
Added chalk and sand [2] . . .	7·64	2·12	1·24	—	12·7

[1] Winton, Ogden and Smith, from Leach, "Food Inspection and Analysis," p. 463, 1920.
[2] Liverseege, Bagnall and Lerrigo, Yearbook of Pharmacy, p. 469, 1926.

(Nomura), and has the odour of salicylaldehyde and the pungent taste of ginger. It dissolves easily in most organic solvents, except light petroleum, but is sparingly soluble in water, and is only slightly volatile in steam. Warmed with concentrated mineral acids the mixture shows a striking series of colours changing from faint yellow to brown, and then deep purple; on adding alkali it becomes blue, green, and finally colourless. Zingerone gives a red colour with Millon's reagent, dissolves to a green solution with alcoholic ferric chloride and reduces ammoniacal silver nitrate. Gingerol and capsaicin (*q.v.*) are both derivatives of guaiacol and are related to vanillin, but whereas the pungent gingerol is hydrolysed by alkalis, yielding products, which possess no pungency, the pungency of capsaicin is unaffected by alkalis. In addition to zingerone, Nomura finds in Japanese ginger a pungent principle *shogaol*, $C_{17}H_{24}O_3$, b.p. 231–238°/15·5 mm.; sp.gr. 1·0448/25°, containing a methoxyl, a hydroxyl and a ketonic group.

Nomura and Tsurumi (Proc. Imp. Acad. Japan, 1927, **3**, 159) have synthesised shogaol by the condensation of zingerone and normal hexaldehyde, and they state that its structure is β-4-hydroxy-3-methoxyphenylethyl *n*-heptenyl ketone. Nomura and his colleagues have endeavoured to establish on what constitutional factors the pungency of the principles in ginger is due and to this end have prepared a large number of homologues of zingerone (Sci. Rep. Tôhoku, 1918, **7**, 67; 1925, **14**, 127, 131, 144, 149; 1927, **16**, 563, 565, 581, 589; 1928, **17**, 693, 695, 703, 707, 973; 1929, **18**, 661; Bull. Soc. chim. 1925, [iv], **37**, 1245; Proc. Imp. Acad. Tokyo, 1926, **2**, 229; 1927, **3**, 159). Most of the derivatives prepared are pungent.

Adulteration.—The only form of adulteration to which whole ginger is subject is the addition of, or substitution by, ginger from which more or less of the strength has been removed by extraction with dilute alcohol or water, in the manufacture of ginger beer, etc.; or with strong alcohol for the preparation of the essence or tincture. Ground ginger may be adulterated by the addition of foreign starches—wheat, maize, rice or turmeric; and, in the past at all events, cayenne pepper and turmeric have been employed to restore the pungency and colour where these have been reduced by the practices already referred to.

Mineral matter, especially calcium carbonate, calcium sulphate and sand may also be present in excess, owing either to their deliberate addition or to their too liberal employment in the preparation of the article.

Ginger preparations have been adulterated with tri-*o*-tolyl phosphate, ethylene glycol and rosin oil, the first-named of which has caused paralysis among those who have taken it (Peter Valaer, J. Amer. Pharm. Assoc. 1930, **19**, 948).

Detection of Adulteration.—The detection of exhausted ginger in small proportion is at present impossible, and even when the amount is substantial the problem is by no means an easy one, because the constituents which are removed by extraction with alcohol and water occur in widely varying proportions, even in different samples of the same kind of ginger, while, in the case of different kinds, the variations are more marked. Tables I and III show this and also the changes in composition brought about by the processes of extraction as commercially carried out.

The most useful determinations for the detection and estimation of exhausted ginger are the ash soluble in water, the alcoholic extract after extraction with ether, and the cold-water extract, and these may with advantages be supplemented by the light petroleum extract or the methyl alcohol extract and a determination of the potash. Microscopic examination is of no assistance and the taste and smell of the sample are of limited utility on account of the great variations in strength of the different kinds of ginger.

No legitimate manufacturing operation affects the analytical results sufficiently to cause any trouble, but it must be borne in mind that the method by which the sample has been extracted, and of which the analyst is usually ignorant, considerably affects the analytical results. (For the effect of exhaustion with alcohol of different strengths, *see* Liverseege, Pharm. J. 1896, [iv], **2**, 112, and for information as to methods of extraction actually employed by ginger beer manufacturers, etc., *see* Dyer and Gilbard, Analyst, 1893, **8**, 200.)

The starchy substances likely to be added to ginger may be detected by the microscope. The unsymmetrical cross observed when ginger starch is viewed under polarised light distinguishes it at once from wheat starch.

Capsicum may be detected by the test suggested by Garnett and Grier (Pharm. J. 1909, [iv], **29**, 441), based on the fact that the pungent flavour of gingerol is destroyed by heating with alkalis whereas that of capsicum is not.

Standards.—The British Pharmacopœia, 1932, requires unbleached Jamaica ginger to be used for official purposes and further requires alcoholic extract (90%) not less than 4·5%, cold-water extract not less than 10%, ash not more than 6% and water-soluble ash not less than 1·7%.

T. McL.

GINGER, ESSENTIAL OIL OF. The oil distilled from the rhizome of *Zingiber officinale* Roscoe (Fam. Zingiberaceæ), indigenous to tropical Asia and cultivated in India, Java, West Indies, Japan and Sierra Leone. The most highly esteemed is the Jamaica variety, where the fibrous roots are removed and the rhizome carefully peeled and scraped and bleached in the sun. The yield of oil is from 1 to 3%. The oil is light yellow in colour and has no pungent taste. The pungent principles of ginger are not volatile in steam.

Constituents.—The main constituent is the sesquiterpene *zingiberene* which boils at 269–270°. Camphene and phellandrene and traces of citral and cineole have been detected. In addition the oil contains a sesquiterpene alcohol *zingiberol*.

Characters.—Sp.gr. 0·876–0·886 at 15·5°, $[\alpha]_D^{20}$ −20° to −50°, n_D^{20} 1·488–1·495, ester value 1–12, after acetylation 30–50.

C. T. B.

GINGERGRASS, ESSENTIAL OIL OF. The oil distilled from *Cymbopogon martini* (var. sofia) Stapf (Fam. Gramineæ), an Indian grass closely allied to *Cymbopogon martini*, var. motia, which yields palmarosa oil. Large areas of gingergrass occur in the dense forests of Melghat, in the Pimpalner and Nandurbar Ranges of the Khandesh district and other ranges of the Nasik district. The oil has a characteristic odour similar to, but quite distinct from, that of palmarosa oil.

Constituents.—The oil contains phellandrene, dipentene and *d*-limonene, geraniol, perilla alcohol and traces of carvone.

Characters.—Sp.gr. 0·900–0·950 at 15·5°, $[\alpha]_D^{20}$ −29° to +22°, ester value up to 30, after acetylation 130–200. Soluble in 3 volumes of 70% alcohol.

C. T. B.

GINGEROL *v.* GINGER.

GINKGO, the fruit of *Ginkgo biloba*, the maidenhair tree of Japan. The yellow plum-like fruit affords a somewhat bitter-flavoured but nourishing food. Langley (J. Amer. Chem. Soc. 1907, **29**, 1513) gives the composition of the kernels as H_2O 15·7, protein 11·0, fat 2·4, starch 57·2, pentosans 1·3, other carbohydrates 8·7, fibre 0·8, ash 2·9%. The protein constituents include a globuline, *ginkgoin*, representing 60% of the total nitrogen, an albumin, a protamine and a glutelin. Furukawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, **24**, 304; 1935, **26**, 178) obtained from the fruit *ginkgol*, $C_{21}H_{34}O$, and *bilobal*, a 3:5-dihydroxypentadecenylbenzene. According to Furuichi (Bull. Tottori Higher Agric. School, 1928, **1**, 105) the ash of the fruit consists of K_2O 40·6, Na_2O 8·4, CaO 4·8, MgO 7·7, Fe_2O_3+Al_2O_3 3·7, P_2O_5 21·6, SO_3 8·3, SiO_2 4·9%.

A. G. Po.

GIRARD'S REAGENTS.—Girard's reagent **T** is the chloride of trimethylacethydrazide-ammonium chloride,

$$Cl[NMe_3{\cdot}CH_2{\cdot}CONH{\cdot}NH_2,]$$

whilst the reagent **P** is the corresponding pyridinium-compound; they are colourless crystalline compounds of (corr.) m.p. 192° and 200° respectively. Reagent **P** is less commonly used, but has the advantage of not being hygroscopic and is more suited to industrial uses.

The reagents are prepared by treating ethyl chloroacetate with trimethylamine or pyridine in alcoholic solution; the betaine so produced is treated *in situ* with hydrazine hydrate (Girard and Sandulesco, Helv. Chim. Acta, 1936, **19**, 1095).

The reagents combine with aldehydes and ketones in presence of acetic acid, forming substituted hydrazones which are water-soluble and are stable for at least 24 hours at p_H 6·5–7 and at low temperatures; the ketonic derivatives are rapidly hydrolysed by mineral acids in the cold with liberation of the ketone, but derivatives of aldehydes are stable under these conditions and are only hydrolysed on heating with high concentrations of mineral acids, preferably in the presence of formalin. This provides a ready means of distinguishing the aldehydic from the ketonic constituents of a mixture.

Alkyl methyl ketones react almost instantaneously, aryl methyl ketones more slowly and diaryl ketones only with great difficulty and on prolonged heating. Cyclic ketones react more slowly than alkyl methyl ketones, whereas $\alpha\beta$-unsaturated ketones react very readily, but the compounds formed are somewhat difficult to hydrolyse; the formation of products of addition of the reagent to the double bond has not been observed. Steric hindrance exercises the same effect as in the formation of semicarbazones; thus, dimethylcamphor does not combine with either reagent **T** or **P**.

The reagents are particularly suited to the isolation of small amounts of ketones contained in various natural products, as, for example, of oestrone from urine (Girard and Sandulesco, *l.c.*) and of the hormones of the suprarenal gland (Reichstein, *ibid.* 1107).

In practice, the ketonic material dissolved in alcohol containing 10% of acetic acid is heated for 30–60 minutes with the reagent in slight excess, the volume being adjusted to give a 10% (or 5%) solution of the reagent. The cooled solution is diluted with ice water containing enough alkali to neutralise nine-tenths of the acid, the solution remaining acid to Bromothymol Blue and containing 10–20% of alcohol. It is extracted with a non-hydroxylic solvent such as ether, which does not dissolve the compounds formed, and the latter are then decomposed by the addition of mineral acid up to a concentration of 0·5*N*.

G. A. R. K.

GIROFLÉ (*v.* Vol. I, 577*a*).

GITALIN (*v.* Vol. II, 384*c*).

GITOXIGENIN (*v.* Vol. II, 382).

GITOXIN (*v.* Vol. II, 384*b*).

GLASERITE (*v.* Vol. I, 450*c*).

GLASS. **Historical.**—Excavations in Egypt and Mesopotamia have yielded fragments that suggest that the peoples of these lands had some knowledge of glazes, if not of glass as such, as far back as 3000–4000 B.C., and a thousand years after this a good deal was known about the making and manipulation of glass. The oldest piece discovered is stated to be a "pearl," 9 x 5·5 mm., from a grave in Thebes of *c.* 3500 B.C. Sir Flinders Petrie gives the date of the earliest glassmaking as 1600 B.C. and certainly by *c.* 1500 B.C. a fairly high standard of technique had been acquired in the making of "pearls," some of which were engraved, and small vessels, these being made by coating a core of clay and sand with glass and then removing the core. The oft-quoted tale of Pliny that the discovery of glassmaking was made by certain Phœnician travellers who used a bag or bags of alkali as a support for a cooking fire in the desert is not now credited, Babylonia being considered by Sir Flinders Petrie to be the home of the art. Although remarkable as an achievement, early work was crude, but when the use of the blowpipe was discovered, probably in Sidon (*c.* 30 B.C.), a great leap forward was made. Sixty years later, workmen from Alexandria were well established in Rome and turning out filigree, mosaic and engraved work, and coloured glass was also known by this time. The Portland Vase, with designs in white on a deep blue base, belongs to the period of A. Severus A.D. 230. Evidence of the use of window glass has been discovered in the ruins of Pompeii, destroyed c. A.D. 70, and it is mentioned by L. A. L. Firmianus in 290, whilst St. Jerome alludes to cast "plate" glass in this connection. There was a colourless window in a Constantinople church by 450, and the first decorated one was in the Lateran Church in Rome in 795. A small amount of glassmaking may have been carried on in Britain during the Roman occupation though conclusive proof of this is not available. In the thirteenth century, the centre of the art moved to Venice, where, at Murano, the industry flourished under State protection until it was killed by the rise of the English lead crystal-glass towards the end of the seventeenth century. The privileged position of the Corporation of Glassmakers in Venice was such that nobles could without loss of rank marry daughters of glassmakers. Heavy penalties were incurred by Venetian glassmakers who went abroad and taught their art to foreigners. The earliest reference to English glass is to some supplied in 1240 for Westminster Abbey by Laurence Vitrearius de Dunkshurstlonde, and another, not very complimentary, is in 1439, when the Countess of Warwick prescribed that no English glass should be used in the windows of the Beauchamp chapel at Warwick. The use of coal in 1610 by Thomas Percival and in 1635 by Sir Robert Mansell, who obtained a monopoly for this, and the development of lead crystal-glass by George Ravenscroft in 1675 led to the rise of the English branch of the art. Workers were introduced from Venice and decoration by cutting was practised by others brought from Bohemia and South Germany at the beginning of the eighteenth century. The brilliant effect produced on lead glass by cutting contributed to the decline in demand for the Venetian ware. In 1696 there was a vigorous industry distributed according to Houghton (Letters) as follows: making bottles, 39 factories; flint, green and ordinary glass, 27; window glass, 15; crown glass and plate, 5; looking glass plate, 2. London was the chief centre of development, whilst Newcastle-on-Tyne was probably next in order of importance.

The first large English factory for making cast plate glass was erected near Prescot in 1773, though the process as we know it originated with Lucas de Nehou in France in 1688. English pressed glass, first made in 1810, was another blow to Continental makers. Progress from this time was connected more and more with the mechanisation of the trade. The first practical bottle-blowing machine was invented by Ashley and Arnall (B.P. 8677 of July 2nd, 1886), and this led in 40 years to the most revolutionary changes in methods. The application by Frederic Siemens in 1856 of the principle of regeneration to waste-heat recovery, modified furnace-design, and 12 years later mass-production methods went forward again, when he built a tank furnace instead of a pot furnace, as had been the practice hitherto. This enabled melting and working to go on simultaneously, so that production could be maintained for 24 hours per day.

In the flat-glass industry, much progress has been made in the past 40 years. The Lubber's method developed from the old mouth-blown cylinder process, good though it was, has been entirely superseded by others in which the sheet is drawn continuously either straight up, or else first upwards and then horizontally, by suitable mechanism (*see later*). In the application of machines to glassmaking generally, America has played a predominant part, although the basic idea in several cases was British. No glassmaking of note was carried on in America before 1800.

The application of scientific methods to glass manufacture may be said to begin, not with Abbe and Schott as is usually claimed, but with the Rev. Vernon Harcourt, some years earlier. In 1834 he carried out a considerable amount of work on the relation of glass composition to physical properties and showed the value of borate and phosphate glasses for optical purposes. Michael Faraday also gave a good deal of attention to optical glass, and realised quite well the need for making experimental meltings in platinum vessels and for stirring carefully to ensure homogeneity sufficient to arrive at optical constants. Abbe and Schott carried on similar work later, and founded in 1884 with Zeiss the famous Jena works, from which came, as a result of their collaboration, thermometer glass, heat and chemical-resisting glass, and those newer optical glasses that have made possible greatly improved microscope lenses (apochromats) and the fast modern photographic objectives. On the practical side, however, the father of the optical glass industry may be regarded as P. L. Guinaud, a Swiss, who with Fraunhofer and Utzschneider in Munich produced lenses larger than any made hitherto. As early as 1790 he introduced the process of stirring glass in order to obtain homogeneity.

As the result of the war (1914–18), glassmaking has developed in a number of new centres. In both Great Britain and America chemical glassware superior to the German product has been produced, and marked progress has been made in England in optical glass of high quality. Japan has built up an extensive glass manufacture, and India is making determined efforts to organise on a better footing the numerous small factories catering for local needs. In South Africa, Brazil, the Argentine and Australia, considerable development has taken place in recent years. Australia in particular among the overseas members of the British Commonwealth is rapidly becoming almost self-supporting in her glass production. Russia is another country in which very great expansion and modernisation of the industry has taken place during the last twenty years.

Definition.—Owing to its complexity and to the large number of possible varieties, glass cannot be brought adequately within the scope of a single or simple definition. It may be defined as an amorphous, hard, brittle substance, usually transparent, but sometimes translucent or even opaque, breaking with a conchoidal fracture and consisting of a material obtained by the fusion of one or more of the oxides, silica, boric oxide, phosphoric oxide and the metallic oxides, followed by sufficiently rapid cooling of the fused mass to prevent crystallisation of the components. The glass may be colourless or may be coloured either by one or more of the constituent oxides or from the effect of neutral bodies such as carbon, sulphur and selenium. According to the definition, glass, being amorphous, will be isotropic. There are some substances, however, which, in certain optical instruments, serve as glasses but are anisotropic in character, and have properties differing in the directions of their crystallographic axes. Such crystalline substances in common use are quartz and calcspar, or Iceland spar.

Most glass technologists regard the term glass as denoting a *state* rather than any given *substance*, and of course many normally crystalline substances like felspar and quartz can be converted by fusion into glasses, and back from glasses to the crystalline state by suitable heat treatment. Developments in what have come to be called Synthetic Plastics have led to some extension of the field covered by the term glass. The two materials inorganic (or pyrogenic) and organic glasses (" plastics ") each have their own special fields of economic usefulness and only compete over a very narrow range.

Properties of Glass.—From their mode of preparation, ordinary glasses must be considered as mixtures of compounds, usually of silicates, but also of borates and, in rarer cases, of phosphates and arsenates. A study of the freezing point curves or equilibrium diagrams of binary and ternary mixtures of silica with other basic oxides has been the most fruitful source hitherto of our knowledge of these compounds probably present in silicate glasses (*see*, for example, Hilpert and Weiller, Ber. 1909, **42**, 2969; 1910, **43**, 2565. Day and Shepherd, J. Amer. Chem. Soc. 1906, **28**, 1,089. Rankin and Merwin, *ibid.* 1916, **38**, 568. H. S. van Klooster, Z. anorg. Chem. 1911, **69**, 122, 127. Shepherd, Rankin and Wright, Amer. J. Sci. 1909, **28**, 293. Rankin and Wright, *ibid.* 1915, **39**, 1. Ferguson and Merwin, Amer. J. Sci. 1918, **46**, 617. Morey and Bowen, J. Phys. Chem. 1924, **28**, 1167; J. Soc. Glass Tech. 1925, **9**, 226. G. W. Morey, F. C. Kracek and N. L. Bowen, J. Phys. Chem. 1929, **33**, 1857; J. Soc. Glass Tech. 1930, **14**, 149; *ibid.* 1931, **15**, 57. F. C. Kracek, J. Phys. Chem. 1930, **34**, 1583, 2461). Wallace (Trans. Ceram. Soc. 1909–10, **9**, 172) and others have claimed that some of these silicates, such as sodium and barium metasilicates, lithium and sodium metasilicate and sodium aluminium trisilicate and calcium aluminium trisilicate (albite and anorthite) form continuous series of solid solutions; and certain others, such as lithium and calcium metasilicates, are soluble only to a limited extent in the solid state, but their work has been questioned.

On rapid cooling, the viscosity of the mass increases greatly and the mixture at length sets, not at any definite temperature, but over an interval which is not easy to define with precision. On reheating, it also softens gradually, and has no melting-point. Accordingly, the commonly prevailing view is that glass is to be regarded as a super-cooled liquid of extremely high viscosity. It is the high viscosity which is the most important factor in preventing the separation in the crystalline form of the compounds present, although it has been suggested that even in apparently transparent glasses, incipient crystallisation may exist, thus explaining, for example, the phosphorescence of fused zinc silicate and bringing glass into line with the behaviour of certain other amorphous substances, such as sulphur, which tend to revert to the stable crystalline state (*see* Jackson, J. Soc. Arts, 1919; S. C. Bradford, J. Soc. Glass Tech. 1919, **3**, 282).

W. H. Zachariasen (J. Amer. Chem. Soc. 1932, **54**, 3481; Phys. Rev. 1932, **39**, 185), B. E. Warren (J. Amer. Ceram. Soc. 1934, **17**, 249; 1935, **18**, 269) and others, as a result of X-ray studies of simple transparent glasses, suggest that the random-network theory of distribution of the atoms in glass gives the best explanation of its behaviour. They are reluctant to admit the possibility of definite compounds occurring, whilst other workers, finding marked breaks in the physical property–composition curves, claim these as evidence of the occurrence of such compounds, leading to the view that molten glasses are solutions of the compounds characterised by the equilibrium diagram for the particular system. In certain cases, *e.g.* opal and ruby glasses, X-ray evidence is quoted as proof of definite substances being present, NaF and $\mathrm{CaF_2}$ in opal glasses, and CdSe in selenium rubies (J. W. Ryde and D. E. Yates, J. Soc. Glass Tech. 1925, **9**, 226; H. P. Rooksby, *ibid.* 1932, **16**, 171).

The general statement made above, in regard to the setting and the softening of glass, is not intended to imply that these processes are absolutely continuous. A. Q. Tool and J. Valasek (Bureau of Standards Papers, 1920, No. 358), indeed, have shown that there is distinct discontinuity in the heating curve of a glass when softening begins, due to slight heat absorption, and a corresponding heat evolution on cooling.

Although ordinary glasses consist of mixtures of compounds, the properties of glasses can, with a considerable degree of success, be referred to the influence of the constituent oxides or added substances; indeed, in some properties there appears to be an additive relationship, as in the case of the density and the coefficient of expansion of sodium–calcium silicate glasses which are of similar molecular type. It must be stressed, however, that the use of relationships involving " factors " for the oxides present in the glass is liable to give calculated results at variance with values determined experimentally if the composition involved differs in type from those from which the factors were deduced. G. Gehlhoff and M. Thomas (Z. tech. Physik, 1926, **7**, 105, 260) gave a series of factors for each oxide studied in their simple glasses in an attempt to correct for the fact that a change in amount of a given oxide from, say, 2–3%, does not produce the same alteration in properties as one from 7 to 8%, but their data still lead to values very far from the truth if indiscriminately applied. The following important properties are discussed mainly on the basis of the effect of the constituent oxides.

Durability. Resistance to disintegrating agents such as water, aqueous solutions of salts, acids or alkalis, atmospheric moisture and dust must be possessed by a glass if it is to be capable of service. Borate glasses and phosphate glasses, whilst possessing valuable optical properties, have hitherto been little used owing to instability in the presence of weathering agents.

TABLE I.—COMPARISON OF EXPERIMENTAL DETAILS OF POWDER METHODS FOR DETERMINING DURABILITY.

Author or method.	Duration of heating (hours).	Quantity of glass powder.*	Grain size mm.	Ratio of limiting grain sizes.	Vol. H_2O (ml.).	Temp. °C.
Mylius [1]	5	20 g., d. 2·584	0·57–0·73	1:1·28	70	Boiling.
Keppeler [2] . . .	5	20 g., d. 2·584	0·62–0·73	1:1·18	70	Boiling.
Peddle [3]	1	5 g.	$<$c. 0·08	1: ∞	100	80
Turner [4]	1	5 g.	0·5–0·8	1:1·6	250	Boiling.
Turner [5]	1	10 g.	0·5–0·8	1:1·6	500	Boiling.
Keppeler and Ippach [6]	5	20 g., d. 2·584	0·116–0·190	1:1·76	100	Boiling.
Fischer and Tepohl [7].	3	1 c.c.	0·15–0·30	1:2	50	80
Enss [8]	7	18 g., d. 2·54	0·5–1·0	1:2	100	100
German [9]	5	10 g., d. 2·5	0·3–0·49	1:1·63	100	100
American No. 1 [10] .	4	10 g., d. 2·5	0·3–0·49	1:1·63	50	90

* Where a density figure is given the glass weight is to be corrected to give the standard volume of glass if of different density.

[1] Ber. 1889, **22**, 310.

[2] "Die Glasfabrikation," 1931.

[3] J. Soc. Glass Tech. 1920, **4**, 36.

[4] Private communication.

[5] J. Soc. Glass Tech. 1922, **6**, 30; 1926, **10**, 304.

[6] Sprechsaal, 1927, **60**, 239.

[7] Glastech. Ber. 1926, **4**, 137.

[8] *Ibid.* 1928, **5**, 449.

[9] J. Soc. Glass Tech. 1928, **12** P, 12, 86, 104.

[10] Bull. Amer. Ceram. Soc. 1935, **14**, 181.

Tests for Durability may be made on the glass in the form of grains or on the glass article as such. In the latter case such factors as the nature of the surface and the ratio of surface exposed to the volume of attacking liquid become important. The many varieties of powder test are indicated in Table I. In all such tests the grains should be of well annealed glass and should be freed from adhering fine dust by blowing with dry air and then washing with dry alcohol until no turbidity is produced, otherwise great difficulty will be experienced in obtaining concordant results (W. E. S. Turner and F. Winks, J. Soc. Glass Tech. 1926, **10**, 102). A boiling test has been specified by the Glass Standards Committee of the Society of Glass Technology for containers in the form of 4 oz. medical bottles (*ibid.* 1931, **15** P, 52) and results of its application described by W. E. S. Turner, H. S. Blackmore, V. Dimbleby, H. S. Y. Gill, H. W. Howes and W. J. A. Warren (*ibid.* 1935, **19**, 171). The results of durability tests are generally specified either as percentage loss in weight or as Na_2O liberated in mg. per sq. dm. or per sq. cm. for surface tests and as Na_2O% or total Na_2O extracted in powder tests. For flat glass, *e.g.* window glass, twin cells are built up by G. Keppeler of three plates and two separators held together to make tight joints and the attacking liquid is placed in the two cells. For glasses of low durability the method of F. Mylius (Z. Instrumentenk. 1888, **8**, 267) uses a solution of 0·5 g. of purified iodeosin in a litre of ether free from acid decomposition products to attack a freshly broken surface for 1 minute. After rinsing in dry ether, the precipitated dye is washed off with 0·1% Na_2CO_3 solution and is determined colormetrically against a standard solution containing 0·01 mg. iodeosin per ml. On this basis Mylius divided glasses into five "hydrolytic classes" h_1–h_5 precipitating 0·00–0·05 0·05–0·1, 0·1–0·2, 0·2–0·4 and 0·4–0·8 mg. iodoeosin per sq. dcm. respectively. The figures for solution from hollow ware of the five classes were, at 80°, 0·00–0·02, 0·02–0·06, 0·061–0·202, 0·202–0·809 and $>$0·809 mg. per sq. dcm. The test does not work so well with borosilicate or glasses containing BaO, PbO or ZnO. A qualitative test that on the Continent has been considered as a quantitative one is that described by L. Kroeber (Chem.-Ztg. 1914, **38**, 1196) using 0·1% solution of narcotine hydrochloride (*see also* J. Soc. Glass Tech. 1923, **7**, 122). The quantity of alkaloid precipitated depends on the amount of alkali liberated by the container.

For testing ampoules a British Pharmacopœa Sub-Committee specify a powder test and one carried out on the ampoules themselves. The latter consists of filling the ampoule with a solution of Methyl Red containing 8·3 ml. of 0·02 *N*-HCl per litre, prepared according to precise directions, sealing and heating in steam to 1 atm. pressure for 30 minutes, cooling and inspecting. The colour of the indicator must not have changed to the full yellow.

The results of powder tests are given in Fig. 1 after V. Dimbleby and W. E. S. Turner (*l.c.*) which compares the behaviour of various oxides on a molecular basis and in Fig. 2 after J. Ensz (Glastech. Ber. 1928, **5**, 1) on a weight per cent. basis. The effect of container-size on results of the 5 hour boiling test for medical bottles (*l.c.*) is apparent from the following table.

EFFECT OF CONTAINER SIZE ON DURABILITY FIGURES FROM BOILING TEST.

Size (oz.).	Area (sq. cm.) / Capacity (ml.)	Alkali liberated.		
		Total mg. Na_2O.	Mg. Na_2O per sq. cm.	Mg. Na_2O per ml. water in test.
1	2·1	0·77	0·013	0·027
2	1·73	1·26	0·012	0·021
4	1·32	2·10	0·013	0·018
6	1·18	2·65	0·013	0·015
8	1·08	3·26	0·013	0·014
12	0·94	4·30	0·013	0·012
16	0·82	4·40	0·012	0·009
20	0·75	5·66	0·013	0·009

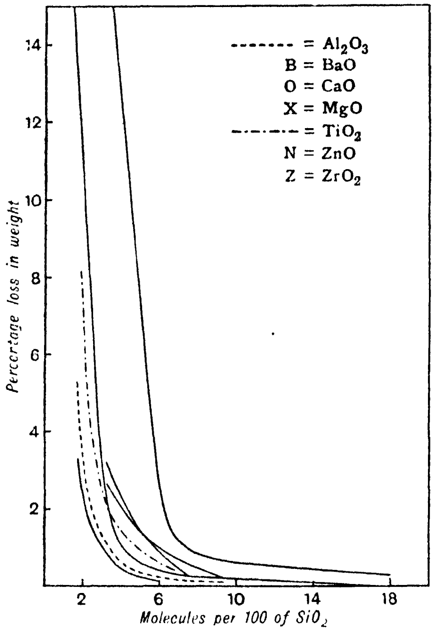


FIG. 1.—EFFECT OF VARIOUS OXIDES ON DURABILITY OF GLASSES OF GENERAL TYPE (MOLECULAR) $6SiO_2(2-x)Na_2O{\cdot}xRO$.

The percentage composition of various bottle glasses (4 oz. medical bottle test) are given below:

Glass.	SiO_2.	R_2O_3.	CaO.	Na_2O.	B_2O_3.	Alkali extracted, mg. Na_2O.
A	74·7	0·3	9·5	14·9	—	2·07
B	73·3	0·8	7·6	16·2	0·7	1·76
C	71·5	1·2	8·8	17·7	0·25	3·7
D	72·0	0·5	9·1	17·5	—	3·9

For the powder test according to the method of Turner and co-workers, bottles should give losses of not more than 0·27% with alkali extracted not more than 0·15%; highly resistant glasses such as chemical ware not more than 0·1 and 0·01% respectively, and lamp-working glasses for ordinary purposes not more than 0·3 and 0·1%. Glass tube used for neon signs needs to be considerably more durable. Comparative values for various types of glass are shown in Table II.

TABLE II.—COMPARATIVE DURABILITIES (POWDER METHOD) OF VARIOUS TYPES OF GLASS.

	Water, % loss.	Constant boiling HCl, % loss.	0·5*N*-Na_2CO_3, % loss.	0·5*N*-NaOH, % loss.
Bottle glass, good . .	0·09	0·08	0·53	1·42
Bottle glass, bad . . .	0·27	0·18	1·78	1·90
Lead crystal glass (22% PbO) . .	0·31	0·37	2·10	3·36
Lead crystal glass (28% PbO) . .	0·16	0·26	1·98	3·20
Chemical ware	0·02–0·06	0·06–0·11	0·22–0·6	1·6–3·9
Gauge glass tubing . .	0·01–0·02	—	—	—
Ampoule tubing	0·01–0·05	—	—	—
Soft lampwork-tubing . .	0·1	—	—	—

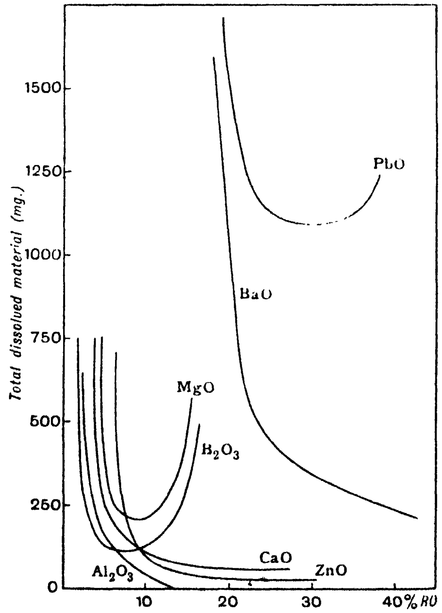


FIG. 2.—EFFECT OF VARIOUS OXIDES ON DURABILITY OF GLASSES OF PERCENTAGE (WEIGHT) COMPOSITION $18Na_2O{\cdot}xRO{\cdot}(82-x)SiO_2$.

Boiler gauge-glasses and similar resistant types may be tested in an autoclave at several atmospheres pressure to obtain results within a reasonable time, but this method does not give results for ordinary glasses in agreement with those of other methods unless the pressures used are very low.

Viscosity is measured by the falling ball method (I. Masson, L. F. Gilbert and H. Buckley, J. Soc. Glass Tech. 1921, **5**, 337; 1932, **17**, 43; A. R. Wood, Ann. Physik, 1934, **21**, 761), Margules rotating cylinder method (E. W. Washburn and G. R. Shelton, Univ. Illinois Bull. 1924, **12**, No. 33; S. English, J. Soc. Glass Tech. 1924, **8**, 205; 1925, **9**, 83; Physical Rev. 1930, **36**, 347) and by drawing out a platinum wire at constant speed from the glass (V. H. Stott, E. Irvine, D. Turner, Proc. Royal Soc. (London), 1926, A, **112**, 499). Viscosities greater than 10^8 poises are measured by observing the rate of deformation of a test piece under some force, *e.g.* torsion, extension under load (S. English, J. Soc. Glass Tech. 1923, **7**, 25; H. R. Lillie, J. Amer. Ceram. Soc. 1931, **14**, 502). Much systematic work still needs to be done to amplify present knowledge. The effect on viscosity at 1,000° of replacing Na_2O by CaO, MgO, Al_2O_3 in the glass $2Na_2O{\cdot}6SiO_2$ is given by S. English as in Fig. 3, and the same worker (*l.c.* 1925, **9**, 83) found in four component glasses derived from Na_2O—CaO—SiO_2 glasses that various substitutes had the effects listed below.

Replacement of	Change in viscosity.						Limit of applicability.
	1,400°C.	1,300°C.	1,200°C.	1,100°C.	1,000°C.	900°C.	
1% Na_2O by 1% SiO_2	+0·040	+0·052	+0·072	+0·083	+0·101	+0·120	—
1% Na_2O by 1% CaO	+0·080	+0·070	+0·062	+0·056	+0·052	+0·048	9% CaO
1% MgO by 1% CaO	+0·097	+0·052	+0·000	+0·022	+0·007	−0·052	1·5% MgO
1% Al_2O_3 by 1% CaO	−0·034	−0·024	+0·010	+0·025	+0·090	+0·20	2% Al_2O_3

Magnesia replacing lime produces at temperatures between 800° and 1,400°C. a definite decrease in viscosity to a minimum (in English's series of glasses at approximately equimolecular amounts of MgO and CaO) and alumina replacing lime gave a steady rise in viscosity at 1,400°, but a well marked drop to a minimum at 1,000° and 800°, this being located at 0·1 molecules Al_2O_3. For a comparison of approximate viscosity values for different types of glass, *see* Table III compiled from the data of C. L. Babcock (J. Amer. Ceram. Soc. 1934, **17**, 329; *cf.* H. L. Crook, J. Soc. Glass Tech. 1939, **23**, 82).

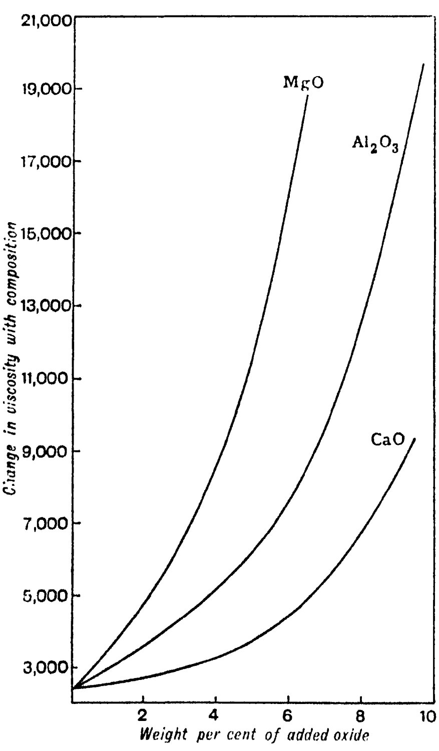


FIG. 3.—EFFECT OF VARIOUS OXIDES ON VISCOSITY OF GLASS.

TABLE III.—VISCOSITY.

Glass.	1	2	3	4	5	6
SiO_2 . .	72·6	67·3	81·0	75	65	60
B_2O_3 .	1·4	2·0	13·0	15	—	—
Na_2O	16·0	14·0	4·0	5	7·5	5
K_2O . .	0·7	—	—	—	7·5	5
MgO . .	1·7	—	—	—	—	—
CaO . .	6·4	7·0	—	—	—	—
ZnO . .	—	7·0	—	—	—	—
PbO . .	—	—	—	5	20	30
Al_2O_3 .	1·0	2·5	2	—	—	—
log η at °C.						
750 .	6·38	6·47	—	—	—	—
850 .	5·30	5·01	—	—	—	—
1,000 .	4·05	3·68	—	—	1·22	1·82
1,100 .	3·45	3·05	1·44	1·25	1·00	1·54
1,200 .	2·82	2·51	1·27	1·04	0·77	1·29
1,300 .	2·46	2·01	1·14	0·87	0·65	1·11

The deformation of glass under load is a function not only of temperature but of time as shown by E. Zschimmer (Silikat-Z. 1914, **2**, 129), who found the cohesion temperature for two polished flat discs of glass fell from 611°C. for 1 minute heating to the following values: 585° (20 minutes), 574° (50), 567° (100), 564° (180), 553° (840), 540° (1,440). Adopting a 30 minute heating time, he found the cohesion temperatures of various optical glasses to be: flints 450–500°, silicate crowns 300–550°, borosilicate crowns 350–600°, barium flints 600–650°, barium crowns 600–700°C. J. T. Littleton (J. Amer. Ceram. Soc. 1927, **10**, 259) defined the

“ softening point ” of a glass as that temperature at which a rod 9 in. long by 0·6 mm. diameter elongates under its own weight at the rate of 1 mm. per minute when its upper 9·5 cm. of length is heated in an electric furnace. This corresponds with a viscosity of 4·5 × 10^7 poises. The Joint Technical Committee of the Society of Glass Technology and the Deutsche Glastechnische Gesellschaft recommended that the maximum point M_g on the thermal expansion curve be taken as the softening point. This may perhaps be regarded as the incipient softening point corresponding with a viscosity of 10^{11}–10^{12} poises. Morey (“ Properties of Glass,” London, Chapman and Hall, Ltd., 1939) considers Littleton's definition agrees better with the usual conception of softening.

Viscosity in Relation to Manipulation of Glass.—The rate of change of viscosity with temperature is very important in glass working. Soda-lime-silica glasses containing a high percentage of lime (12–14% CaO) set very quickly as the temperature falls. They are thus suited to hand production of bottles and the drawing of sheet glass. Mechanical bottle production requires a glass with less rapid setting characteristics or a longer “ working range ” so lime is replaced by alkali and to some extent by magnesia whilst a little silica is sometimes replaced by alumina. Where complicated manipulation in hand processes is carried out as in making lead crystal-tableware, the very large working range of the potash–lead glasses is exploited. The temperatures corresponding to the following viscosity values are of importance in manipulation: 10^3 C.G.S. units (average furnace working temperature), 10^6 C.G.S. units (lower limit of working range), and approximately 10^{13} C.G.S. units (the temperature at which a break occurs in the temperature–property curve).

Surface Tension is of importance in several manufacturing processes, notably in the heating of thin walled vessels, *e.g.* melting off the caps of electric lamp-bulb blanks, sealing the pinch assembly into the bulb, fire-finishing tumbler edges. Most of the somewhat scanty and unsystematic work done has been by the drop-weight method which gives rapid and comparable rather than precise values (E. W. Tillotson, Ind. Eng. Chem. 1911, **3**, 631; 1912, **4**, 651), but recently the bubble method has been used (F. M. Jaeger, Z. anorg. Chem. 1920, **101**, 1. C. W. Parmelee and co-workers, J. Amer. Ceram. Soc. 1937, **20**, 224, 235; J. Soc. Glass Tech. 1937, **21**, 44; Univ. Illinois Bull. 1939, **36**, No. 311. G. Keppeler, J. Soc. Glass Tech. 1937, **21**, 53). Considerable discrepancy of results exists between observers. The best values for ordinary silicate glasses are around 300 dynes per cm. The temperature coefficient is low, namely −0·01 to −0·04% per °C. Borate and lead glasses have a lower surface tension than alkali or alkaline earth silicates.

Density or rather **Specific Volume** is an approximately additive property so that factors may be assigned to be used in the Winkelmann formula $100/D=P_1/d_1+P_2/d_2+$, etc., where D is the density of the glass, P_1, P_2, . . . the percentage amounts of the constituent oxides and d_1, d_2, . . . the density factors assigned to them. The various factors deduced are given below.

Oxide.	Winkelmann and Schott.	Baillie.	English and Turner.	Tillotson.
SiO_2 .	2·3	2·24	2·2	2·3
B_2O_3 .	1·9	—	—	—
Na_2O .	2·6	3·2	3·47	—
K_2O .	2·8	—	—	—
MgO .	3·8	3·25	3·38	4·0
CaO .	3·3	4·3	5·0	4·1
ZnO .	5·9	—	—	—
BaO .	7·0	—	—	—
PbO .	9·6	—	—	—
Al_2O_3 .	4·1	2·75	2·75	2·75
P_2O_5 .	2·55	—	—	—
Li_2O .	—	—	—	—

Determination.—(1) Displacement method of Archimedes; (2) flotation of grains in mixed liquids adjusted until the grain neither sinks nor floats, followed by a determination of the density of the liquid (capable of high precision and applicable to very small amounts); (3) pyknometer method (liable to error from entrapped air).

Past thermal history affects the density. G. W. Morey and H. E. Merwin (J. Opt. Soc. Amer. 1932, **22**, 632) found that differences of 0·006–0·011 occurred between well annealed specimens and those which had been quickly cooled, the former having the higher values. To reach the maximum density a few hours annealing at 200–300° below the temperature of “ incipient flowage ” was found necessary. Little is known of the density of glass at temperatures beyond the softening point. S. H. Li (Univ. Illinois Bull. 1924, No. 140) gave the following:

SiO_2.	Na_2O.	CaO.	Density at	
			1,206°C.	1,454°C.
82·6	17·4	—	2·19	2·15
70·0	30·0	—	2·42	2·41
60·0	40·0	—	2·28	2·35
63·0	13·6	23·4	2·61	2·59
70·0	20·0	10·0	2·26	2·20
70·0	10·0	20·0	2·31	2·23
72·25	15·1	12·1	2·28	2·23
73·5	16·5	10·0	2·31	2·28

W. Hänlein (Glastech. Ber. 1932, **10**, 126) found a drop from 2·28 at 800° to 2·185 at 1,400°, whilst G. Heidtkamp and K. Endell (*ibid.* 1936, **14**, 89) found a drop from 2·27 at 1,000° to 2·22 at 1,400° for a 20% Na_2O and from 2·26 to 2·14 for a 60% Na_2O soda-silica glass. *See also* I. Sawai and S. Inoue, J. Soc. Chem. Ind. Japan, 1940, **43**, 47B.

The densities of the system

$$Na_2O—CaO—SiO_2$$

according to F. C. O. Glaze, J. C. Young and

A. N. Finn (Bur. Standards J. Res. 1932, **9**, 799) may be represented by the formula

$$1/D=aA+\beta B+\gamma C+\gamma' C^2$$

where A, B and C are the percentages of SiO_2, Na_2O and CaO respectively, and a, β, γ and γ' are "constants" chosen according to the following table:

Silica limits per cent.	$a\times10^3$.	$\beta\times10^3$	$\gamma\times10^3$.	$\gamma'\times10^6$.
50–A_a*.	4·252	3·537	2·545	8·0
A_a–A_b .	4·3028	3·4628	2·500	4·0
A_b–A_c .	4·3922	3·2872	2·285	5·0
A_c–100 .	4·5400	2·8460	1·844	14·8

*$A_a=59·4-0·23(\%CaO)+0·032(\%CaO)^2$.
$A_b=66·3+0·15(\%CaO)-0·004(\%CaO)^2$.
$A_c=74·9-0·017(\%CaO)^2$.

The densities of a number of glasses are given in Table IV (p. 544) which also includes optical data.

Thermal Expansion is measured by the expansion of a rod relative to a comparison specimen of known behaviour (Chevenard method used by Turner and Winks, J. Soc. Glass Tech. 1928, **12**, 57) using an optical lever system; by interferometer methods (C. G. Peters and C. H. Cragoe, Bur. Stand. Sci. Papers 1920, No. 393; R. Wenig and E. Zschimmer, Sprechsaal, 1929, **62**, 853) or by mercury in a glass volumenometer (S. English and W. E. S. Turner, J. Soc. Glass Tech. 1919, **3**, 238). The form of the expansion curve is shown in Fig. 4 from Turner and Winks (*ibid.* 1930, **14**, 90), the lowest curve being that of a highly strained specimen. The expansion in the annealing range is from 2 to 11 times the rate in the lower range (Peters and Cragoe, J. Opt. Soc. Amer. 1920, **4**, 105). Below the lower annealing temperature T_g the linear expansion may be calculated by the factors of English and Turner (J. Amer. Ceram. Soc. 1927, **10**, 551; 1929, **12**, 760), namely SiO_2 05, B_2O_3 (up to 12%) 6·53, Na_2O 41·6, K_2O 39·0, MgO 4·5, CaO 16·3, ZnO 7·0, BaO 14·0, PbO 10·6, Al_2O_3 4·0, all multiplied by 10^{-8}. These are used in the formula $a=a_1p_1+a_2p_2\ldots$ where a_1, a_2 are the factors for the oxides and p_1, $p_2\ldots$ the percentage amounts present, replacing the classic ones of Winkelmann and Schott. The existence of definite change points on the expansion curves below T_g is reported by Turner and Winks (*l.c.*), A. Klemm and E. Berger (Glastech. Ber. 1927, **5**, 405), E. Seddon and W. E. S. Turner (J. Soc. Glass Tech. 1933, **17**, 324), but questioned by J. T. Littleton (*ibid.* 1931, **15**, 262). The past thermal history undoubtedly affects behaviour in this range. J. B. Saunders and A. Q. Tool (Bur. Standards J. Res. 1933, **11**, 799) found for a Pyrex glass that the linear expansion between 20 and 200° could be altered 10% by heat treatment in the range 450–750°C. In general, quickly cooled glass has a higher expansion up to some temperature below T_g (called D_t by Turner and Winks, *see* Fig. 4) than that of a well annealed specimen. Values for the linear expansion coefficients $a\times10^7$ of some industrial glasses are Pyrex glass 32–36 (between 21–471°C.), Jena 59^{III} 64 (38–522°), Jena laboratory ware 48 (19–414°), gauge glass 46, bottle glass 82–88 (20–100°), plate glass 88 (0–400°), lead crystal glass 88.

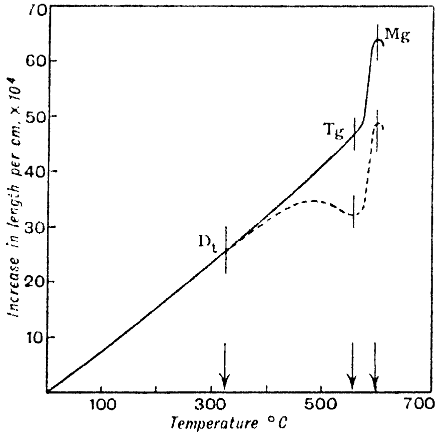


FIG. 4.—THERMAL EXPANSION CURVES. STRAINED SPECIMEN SHOWN DOTTED.

When two glasses have to be sealed together as in lamp-working or the casing of coloured glass on a colourless base, or when wires are sealed into glass, not only should the expansion coefficients of the two substances agree fairly well, but there should be matching of the characteristics over the annealing range of the glasses (W. E. S. Turner and F. Winks, J. Soc. Glass Tech. 1928, **12**, 25, 57, 161; A. W. Hull and E. E. Burger, Physics, 1934, **5**, 384; C. J. Milner, J. Soc. Glass Tech. 1939, **23**, 308).

The success of the sealing operation depends upon the angle of contact of glass and metal and on the nature and thickness of the latter. When two glasses are sealed together the thickness of the two layers (as in flashed or cased opal) is of importance.

Specific Heat is more nearly an additive property than any other. A. Winkelmann (Ann. Phys. Chem. 1893, [iii] **48**, 401) gave as the relation

$$C_p=\frac{p_1c_1}{100}+\frac{p_2c_2}{100}+\ldots$$

where $p_1p_2\ldots$ are the percentage amounts of individual oxides present and c_1c_2 their specific heat factors. The latter he gave as SiO_2 0·1913, B_2O_3 0·2272, P_2O_5 0·1902, Na_2O 0·2684, K_2O 0·1860, Li_2O 0·5497, CaO 0·1903, BaO 0·0673, ZnO 0·1248, PbO 0·0512, MgO 0·2439, Al_2O_3 0·2074. A. Thuret (J. Soc. Glass Tech. 1936, **20**, 680) gave the mean specific heat of fused silica as

$$C_m=\frac{at+Co,}{bt+1}$$

where $a=0·4579\times10^{-3}$, $b=1·4747\times10^{-3}$, $Co=0·1683$ and t=temperatures between 1,200° and +2,600°C.

TABLE IV.—DENSITY AND OPTICAL PROPERTIES OF DIFFERENT TYPES OF GLASS.

Type.	SiO_2.	B_2O_3.	Al_2O_3.	MgO.	CaO.	BaO.	ZnO.	PbO.	Na_2O.	K_2O.	d_{20}.	n_D.	n_F-n_C.	ν.*
Fused silica	100·0	—	—	—	—	—	—	—	—	—	2·203	1·4585	—	—
Soda silica	50·0	—	—	—	—	—	—	—	50·0	—	2·5656	1·5163	—	—
" "	70·0	—	—	—	—	—	—	—	30·0	—	2·4644	1·5021	—	—
" "	80·0	—	—	—	—	—	—	—	20·0	—	2·3813	1·4898	—	—
Soda lime silica	72·1	—	—	—	13·7	—	—	—	14·2	—	2·5276	1·5265	—	—
" " "	74·1	—	—	—	10·7	—	—	—	15·2	—	2·4935	1·5182	—	—
" " "	70·0	—	—	—	10·0	—	—	—	20·0	—	2·525	1·5231	0·00905	—
" " "	75·5	—	—	—	9·3	—	—	—	15·3	—	2·4734	1·5135	—	—
Alkali lead oxide silica	55·9	—	0·2	—	0·3	—	—	32·9	—	11·1	3·07	1·5632	0·0131	42·9
" " " "	45·0	—	—	—	—	—	—	49·3	0·8	10·0	3·553	1·6157	0·0169	36·4
" " " "	38·1	—	—	—	—	—	—	52·5	9·4	—	—	1·6694	0·0346	31·3
" " " "	24·9	—	—	—	—	—	—	72·9	1·6	0·2	5·395	1·8342	0·0348	24·0
" " " "	20·5	—	—	—	—	—	—	78·9	0·4	—	6·017	1·9163	0·0436	21·0
" " " "	7·99	—	—	—	—	—	—	90·04	1·8	—	7·21	2·179	0·0988	11·9
Potash lime silica	80·0	—	—	—	5·0	—	—	—	—	15·0	2·371	1·493	0·0078	—
" " "	72·5	—	—	—	10·2	—	—	—	—	17·3	2·448	1·510	0·0084	—
Soda potash lime silica	70·0	—	—	—	15·0	—	—	—	7·5	7·5	2·534	1·5307	0·00882	—
" " " "	70·0	—	—	—	10·0	—	—	—	10·0	10·0	2·509	1·5206	0·00876	—
Fluor crown	54·8	18·7	0·3	($F_2=7·5$)	—	—	—	—	—	20·3	2·47	1·4785	0·00682	70·2
Borosilicate crown	69·6	6·7	0·3	—	2·9	—	—	—	—	20·5	2·46	1·5087	0·00793	64·1
Dense barium crown	32·3	19·0	5·7	($As_2O_3=0·5$)	0·2	42·3	—	—	—	0·2	3·31	1·5881	0·00962	61·1
Hard crown	72·0	—	0·3	—	11·4	—	—	—	6·1	10·1	2·49	1·5186	0·00860	60·3
Medium barium crown	45·6	4·4	4·9	($As_2O_3=0·6$)	0·3	32·5	7·9	—	—	3·9	3·23	1·5774	0·0099	57·7
Light barium flint	47·5	—	0·2	—	0·3	15·3	8·3	16·3	3·9	9·1	3·06	1·5523	0·0108	51·4
Light flint.	59·7	—	0·3	—	0·3	—	—	26·9	—	12·6	2·93	1·5472	0·0120	45·8
Dense flint	48·0	—	0·2	—	0·3	—	—	45·1	5·2	1·2	3·55	1·6134	0·0166	36·9
Extra dense flint	40·6	—	0·2	—	0·2	—	—	51·5	—	7·5	3·87	1·6469	0·0192	33·7
Double extra dense flint . . .	35·1	—	0·1	—	0·1	—	—	61·8	—	2·8	4·47	1·7167	0·0243	29·5
Fused boric oxide	—	100·0	—	—	—	—	—	—	—	—	1·812	1·4582	0·0078	58·8
Telescope flint	52·4	18·3	1·9	($Sb_2O_3=20·4$)	0·3	—	—	—	2·3	4·3	2·67	1·5237	0·0100	52·2

* $\nu=\dfrac{n_D-1}{n_F-n_C}$

The values of C_t for Pyrex glass are given as $0{\cdot}174+0{\cdot}00036t$ by J. H. Hildebrand, A. D. Duschak, A. H. Foster and C. W. Beebe (J. Amer. Chem. Soc. 1917, **39**, 2293), and as $0{\cdot}1839+0{\cdot}0003134(t-20)$ by T. De Vries (Ind. Eng. Chem. 1930, **22**, 617). Values for some commercial glasses given by C. W. Parmelee and A. E. Badger are reproduced below, values being in " 20° calories " per gm. per °C. (Univ. Illinois Bull. 1934, No. 271).

	Glass.								
	1.	2.	3.	4.	5.	6.	7.	8	9.
SiO_2	74·1	71·88	73·28	74·95	71·58	74·84	61·91	80·10	67·53
B_2O_3								12·60	
Na_2O	16·65	17·59	16·31	15·82	14·00	16·48	8·32	4·17	8·48
K_2O	0·04						6·19	0·15	3·25
CaO	4·65	5·01	5·31	4·79	12·94	2·55	trace	0·02	10·48
MgO	3·23	3·64	3·88	3·30	0·10	1·77	trace		
PbO							22·23		0·097
Al_2O_3	0·33	1·21	0·48	1·13	0·54	4·36	1·00	1·92	6·01
Fe_2O_3	0·065	0·07			0·12		0·15	0·077	0·081
Heat capacity 40–800°	0·280	0·268	0·280	0·265	0·274	0·279	0·211	0·271	
Heat capacity 40–1,000°	0·292	0·290	0·285	0·293	0·289	0·281	0·224	0·287	0·269

Thermal Conductivity has not been widely studied. Probably the most systematic survey was that of A. Russ (Sprechsaal, 1928, **61**, 887) who worked on the Gehlhoff and Thomas glasses of general percentage composition alkali 18, oxide 82 (SiO_2+RO or R_2O_3). From the results he obtained " factors " using the Winkelmann formula

$$\frac{100}{\lambda}=\frac{b_1}{\lambda_1}+\frac{b_2}{\lambda_2}+\frac{b_3}{\lambda_3}$$

in which λ is the reciprocal of conductivity, and b_1, b_2, etc., the volume percentages. The factors were as follows, the density factors used being given in brackets: SiO_2 3(2·3), B_2O_3 3·7(2·1), Na_2O 10·7(3·2), K_2O 13·4(2·9), CaO 8·8(3·9), BaO 11·85(7·1), ZnO 8·65(5·9), PbO 11·7(10·0), MgO 4·55(3·9), Al_2O_3 6·25(3·2). Pyrex chemical glass has a conductivity between −181° and +250°C. $K=A+b\log_{10}T$ where A and b have the values −0·003523 and +0·002454 respectively and T is the absolute temperature (R. W. B. Stephens, Phil. Mag. 1932, [7], **14**, 897).

Thermal Endurance is the measure of resistance of a glass to sudden changes in temperature. It is of a complex nature depending on thickness, mechanical strength, diffusivity and thermal expansion. Classical work was done by Winkelmann and Schott (Ann. Phys. Chem. 1894, [iii], **51**, 730) who, working on cubes of glass, gave the expression for the shock

$$\theta_c-\theta_0=\frac{P\sqrt{D}}{aE}$$

where P is tensile strength, a linear coefficient of thermal expansion, E is Young's modulus and D diffusivity (=thermal conductivity divided by the product of specific heat and density). V. H. Stott (J. Soc. Glass Tech. 1924, **8**, 139) gave

$$\theta_c-\theta_0=\frac{P(1-\sigma)}{aE}$$

where σ is Poisson's ratio. This did not involve conductivity. C. E. Gould and W. M. Hampton (*ibid.* 1930, **14**, 188) using beakers as test material gave $\theta\sqrt{2b}=B$ (a constant) where θ was the temperature drop to cause fracture and $2b$ was the maximum thickness along the bottom fracture. W. J. A. Warren (*ibid.* 313) modified this to $B=\theta l^n$ where l was thickness and n varied with thickness between 0·36–0·4 for thickness of 1·4 mm. reaching 0·5 for thickness of 1·1 mm.

Determination.—(1) By heating wax in a beaker of standard form and plunging into cold water at 15°C., repeating from successively increased temperatures (5° steps) till fracture occurs (for details, *see* J. Soc. Glass Tech. 1930, **14**, P, 160). (2) Dropping rods 1 in. long from a vertical heating furnace one at a time into water and repeating from higher temperature till fracture occurs (*ibid.* 1933, **17**, 239; 1936, **20**, 498). (3) Standing articles such as jam jars in a stream of running cold water and filling with hot water starting with the jars next the cold water exit (J. B. Murgatroyd, *ibid.* 1932, **16**, 1; 1936, **20**, 511) or slowly heating water inside (*ibid.*). (4) Heating containers totally immersed in a bath of hot water to a constant temperature, removing and plunging into a bath of cold water whilst still full of hot (*see* J. Soc. Glass Tech. 1940, **24**, P, 75).

In all such methods a strict schedule of operation must be followed, and the testing must be done on a statistical basis using large numbers of specimens to eliminate the effect of " freak " results. Standard test procedures have still to be agreed upon. The form of the article tested has considerable influence. Fire-rounding the edges of test rods in (2) above gave much less scattering of results, and R. W. Douglas (*ibid.* 1936, **20**, 517) pointed out the effect of shape in setting up thermal stresses even in well annealed illuminating ware. He favoured dropping water on such specimens under service conditions. For testing tubing he recommended forcing cold mercury into the heated tube as giving closer agreement with behaviour in practice than water immersion tests.

Effect of Composition.—In test (1) above chemical ware beakers withstood a temperature shock of 239–209°C. whilst beakers of sheet glass withstood only 126°C. In the rod test, a commercial lime-soda glass gave values of approximately 131°, 125° and 115° for diameters of 3–4, 4–5 and 5–6 mm. respectively, whilst a " soft soda " glass as used for lamp-working gave in the same size groups values of 112°, 104° and 96° and a commercial borosilicate glass gave values of 325°, 308° and 285°.

Optical Properties.—*Refractive Index* is generally expressed for the mean sodium (D) line (5,893A), but the mercury lines *h*(4,047A), *g*(4,358), hydrogen G′(4,341), F(4,861), C(6,563), helium (4,922), *b*(7,065), *d*(5,876) and potassium A′(7,682) lines are also used. For optical computation the differences in the refractive indices for various wave-lengths is needed and this is expressed either as a direct difference, *e.g.* $n_F - n_C$ often written F−C or as the quantity $\nu = (n_D - 1)/(n_F - n_C)$. Optical data on simple glass systems are not very complete, most accurate measurements having been made on special glasses for optical purposes. For a " series " of glasses of the same type, refractive index and density move in parallel. Specific refractivity is given by the following formulæ: Gladstone and Dale $(n-1)/d$; Lorentz and Lorenz $(n^2-1)/(n^2+2)d$, Eykman $(n^2-1)/(n+0{\cdot}4)d$ and Lichtenecker $(\log n)/d$. G. W. Morey and H. E. Merwin (J. Opt. Soc. Amer. 1932, **22**, 632) give for the soda-lime-silica glasses the formula for calculating specific refractivity according to (*a*) Gladstone and Dale as

$$0{\cdot}1947(\%\mathrm{Na_2O}) + 0{\cdot}2268(\%\mathrm{CaO}) + 0{\cdot}2081(\%\mathrm{SiO_2})$$

and (*b*) Lorentz and Lorenz as

$$0{\cdot}1115(\%\mathrm{Na_2O}) + 0{\cdot}1221(\%\mathrm{CaO}) + 0{\cdot}1237(\%\mathrm{SiO_2}).$$

The Gladstone and Dale formula gave the better results. In three-component glasses ZnO has about the same effect on dispersion as CaO for the same percentage weight, but only about half as much on refractive index; BaO has less effect than PbO on both refraction and dispersion and for a given change in refractive index the change in dispersion is less than for the corresponding PbO glass. For equal weight percentages

$$\mathrm{Bi_2O_3—Na_2O—SiO_2}$$

glasses have higher indices than corresponding PbO glasses. $\mathrm{K_2O—CaO—SiO_2}$ glasses have lower index dispersion than corresponding $\mathrm{Na_2O}$ glasses. The same holds for $\mathrm{K_2O—BaO—SiO_2}$ and $\mathrm{Na_2O—BaO—SiO_2}$ glasses. Mixed alkali-lead and mixed alkali-barium glasses have intermediate properties. In the optical glasses $\mathrm{B_2O_3}$ shortens the violet spectrum, the borate flints having highest red and lowest violet dispersions. Total dispersion increases from the borate crowns ($\mathrm{Al_2O_3}$ and $\mathrm{B_2O_3}$) to the borate flints (PbO and $\mathrm{B_2O_3}$), intermediate glasses having notable amounts of BaO and/or ZnO. Borosilicate flints come between borate and silicate flints. Fluorine (6–9%) decreases the F—C value without affecting greatly the partial dispersion ratios. Data for n_D and F—C values have been given in Table IV, also composition and densities. The effect of rise in temperature is to increase refractive index up to the annealing region (A. A. Lebedeff, Trans. Opt. Inst. Petrograd, 1921, **2**, No. 10; C. G. Peters, Bur. Stand. Sci. Papers 1926, No. 521). In passing through that region a rapid falling off occurs.

Stress-Optical Properties.—D. Brewster (Trans. Roy. Soc. London, 1816) showed that glass under stress behaves as a uniaxial optically negative crystal, the birefringence being proportioned to the stress. L. H. Adams and E. D. Williamson (J. Franklin Inst. 1920, **190**, 597, 835) have discussed mathematically the stresses developed in glass by temperature gradients and the resulting birefringence. S. R. Savur (Phil. Mag. 1925, **50**, 453) measured the stress-optical coefficient in tension and in compression and stated that up to stresses of 100 bars (1 bar=10^6 dynes per cm.^{2}) the relation between stress and birefringence is linear, being the same for tension and compression. The unit proposed for photoelasticity is the Brewster=a relative retardation of 1 Ångstrom unit per mm. per bar.

F. Pockels (Ann. Physik. 1902, [iv], **7**, 745) found that the stress-optical effect diminished regularly in lead glasses with increase of PbO. The ordinary effect was negative but with higher PbO content it became positive and Pockels estimated that a glass of composition $\mathrm{SiO_2}$ 22·8, $\mathrm{K_2O}$ 1·5, PbO 75·7 would have a zero value. L. N. G. Filon and co-workers (Proc. Roy. Soc. London, 1922, A, **101**, 165; 1931, A, **130**, 410) found values for the stress-optical coefficient ranging from 1·8 for a heavy silicate flint to 3·66 for borate flint.

The absorption of light is dependent partly on the thickness, but mainly on the composition of the glass, especially in respect of its content of oxides which exercise selective absorption. The best optical glass should transmit 98–99% of the light passing the surface on which it falls. On the other hand, unpolished mirror glass, 8 mm. thick, may only transmit about 87%, whilst for glass strengthened by wire mesh, the transmitted light may be only 55–60%. The foregoing refers to general transmission of ordinary white light. In the case of selective absorption, the different coloured oxides vary in the strength of their effect, cobalt oxide being one of the most powerful. The absorption curves for several glasses containing CoO, $\mathrm{Cr_2O_3}$, NiO, $\mathrm{Fe_2O_3}$ and $\mathrm{Mn_2O_3}$ have been measured by Zsigmondy (Ann. Physik. 1901, **4**, 60).

The selective absorption varies both with the concentration of the oxide and with the temperature. The general effect of rise of temperature is to shift the absorption towards the red end whilst the amount of absorption may simultaneously be increased. This is illustrated by the following relative transmission factors at different temperatures (M. Luckiesh, J. Amer. Ceram. Soc. 1919, 2, 743) :

Colouring agent.	Colour.		Relative transmission factor.		
	(1) Cold.	(2) Hot.	30°.	200°.	350°.
Cu .	Medium red	—	100	92	84
Co .	Light blue	—	100	104	108
Co .	Deep violet	Deep blue	No appreciable change		
Au .	Pink	Violet	100	96	93
Cu .	Bluish-green	Yellowish-green	100	94	82
Mn .	Purple	Bluish-violet	100	94	90
Cu .	Deep red	—	100	67	42
Cr .	Yellowish-green	Yellow	100	81	67

More recent work by A. J. Holland and W. E. S. Turner (private communication) deals with a series of commercial and other glasses of known composition. Data for three such glasses are reproduced in Figs. 5, 6 and 7, the calculated percentage compositions being shown in the table :

Glass.	Optical D.E.D.F.	Green bottle.	Selenium ruby.
SiO_2 . . .	26·9	68·5	68·1
B_2O_3 . . .	—	—	11·7
PbO	71·9	—	—
ZnO	—	—	11·6
Al_2O_3 . . .	—	3·4	1·3
Fe_2O_3 . . .	0·01	1·6	0·03
MnO_2 . . .	—	2·3	—
CaO . . .	—	8·9	—
MgO . . .	—	0·3	—
Na_2O . . .	—	15·4	5·7
K_2O	—	—	0·3
As_2O_3 . . .	0·1	—	—
$(CdS + Se)$ . .	—	—	1·3

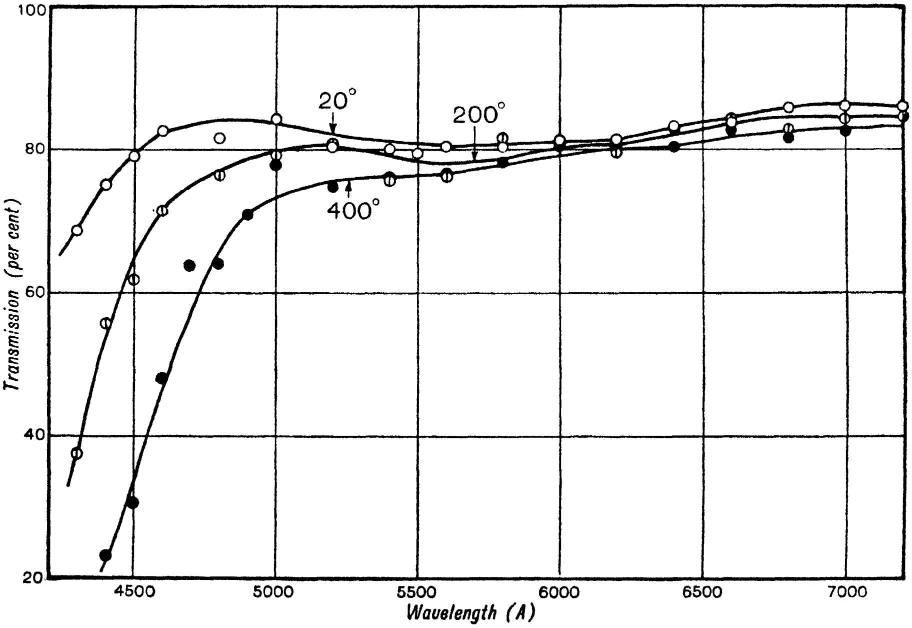


Fig. 5.—Effect of Temperature on Spectral Transmission of a Double Extra Dense Flint Optical Glass (thickness 10 mm.).

In regard to ultra-violet radiation, fused quartz and fused B_2O_3 are transparent, whilst a mixture of B_2O_3, CaF_2 and Al_2O_3 shows only weak absorption. Heavy lead-glasses and glasses coloured slightly with Cr_2O_3 absorb ultra-violet light.

Glasses which absorb heat radiations may be obtained by the use of the oxides or other compounds of chromium, cerium and iron, and certain other elements. The mineral biotite and the oxide Fe_3O_4 dissolved in soda-lime glass absorb a high proportion of incident heat rays, whilst Crookes prepared a soda-lime glass from a batch containing 10% of ferrous oxalate which absorbed 98% of the heat radiations (Crookes, Phil. Trans. 1914, **214**, 1).

Absorption and Transmission have been studied by R. Zsigmondy (*l.c.*), G. Gehlhoff, M. Thomas

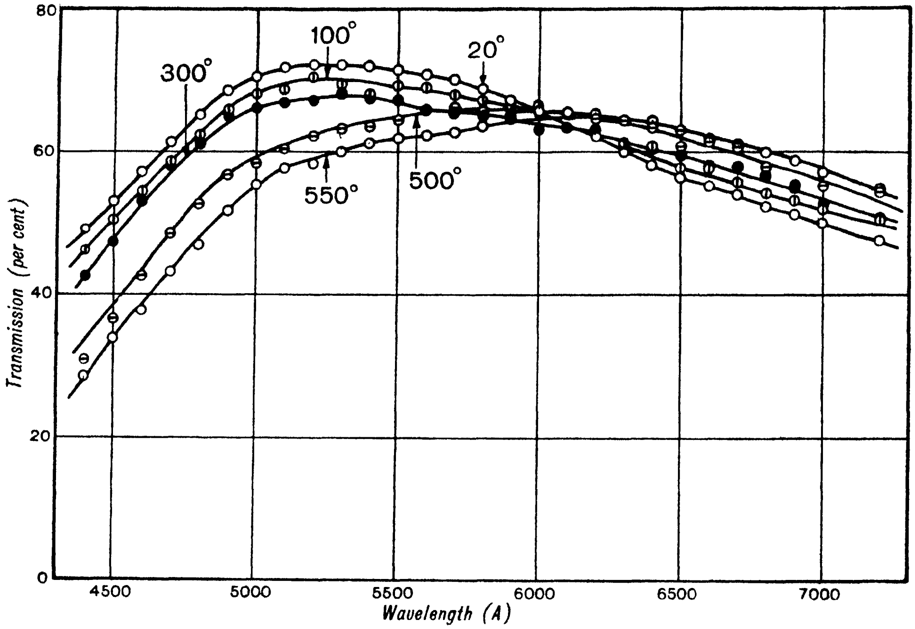


FIG. 6.—EFFECT OF TEMPERATURE ON SPECTRAL TRANSMISSION OF AN IRON MANGANESE DARK GREEN BOTTLE GLASS (THICKNESS 2 MM.).

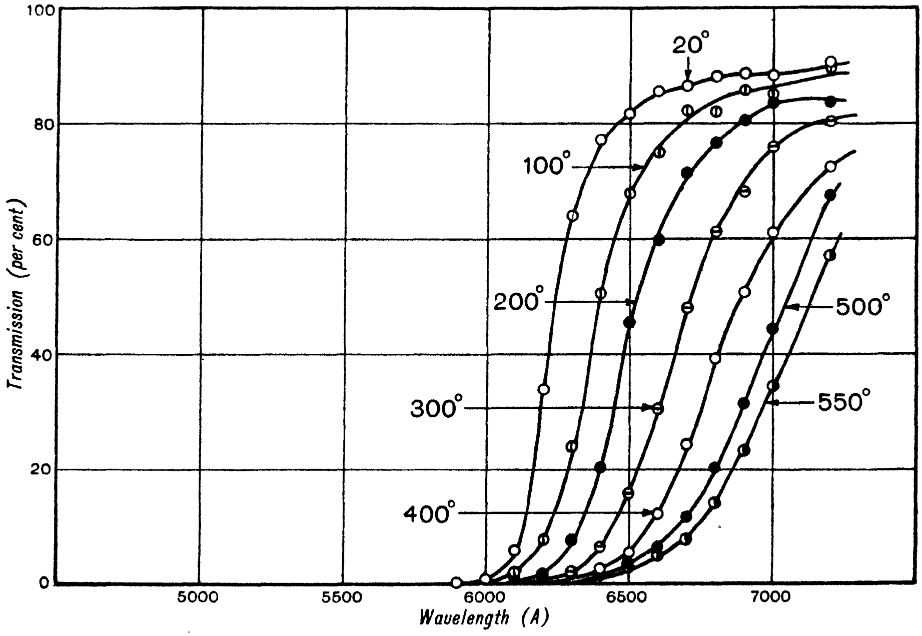


FIG. 7.—EFFECT OF TEMPERATURE ON SPECTRAL TRANSMISSION OF A SELENIUM RUBY GLASS (THICKNESS 2 MM.).

and Fritz Schmidt (Z. tech. Physik, 1930, **11**, 289), W. Weyl (Glastech. Ber. 1931, **9**, 641; 1933, **11**, 67, 113). The results are set out in curve form, Figs. 8 and 9, and in Tables V, VI and VII. For spectral transmissions of eye-protecting glasses, *see* W. W Coblentz and R. Stair (Bureau Standards Circular C. 421) and Optician Supplement, April 14th, 1939.

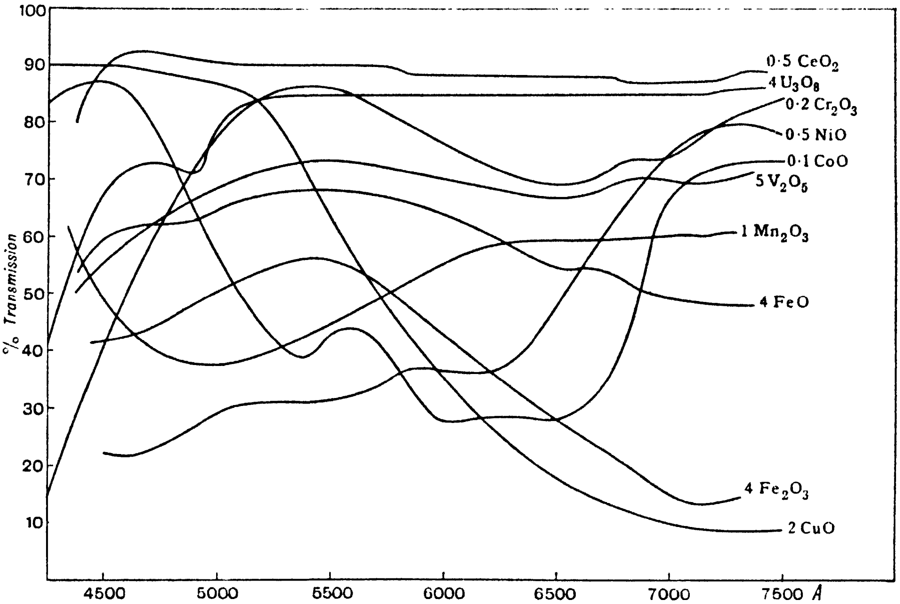


FIG. 8.—TRANSMISSION CURVES FOR VARIOUS COLOURED GLASSES—VISIBLE REGION.

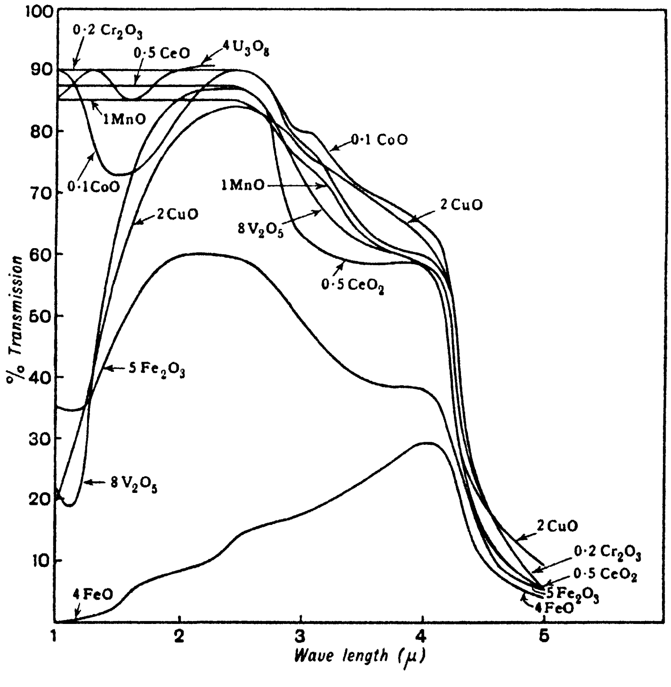


FIG. 9.—INFRA-RED TRANSMISSION CURVES FOR VARIOUS COLOURED GLASSES.

TABLE V.

A. SPECTRAL TRANSMISSION OF SOME OPTICAL CONTRAST FILTERS 2·0 MM. THICKNESS—VISUAL RANGE.

	Transmission %. λ (mμ).									
	300.	350.	400.	450.	500.	550.	600.	650.	700.	750.
Ruby 1	0	0	0	0	0	0	0·4	65	92	92
Red 2	0	0	0	0	0	0	17·5	92	92	92
Deep orange . . 3	0	0	0	0	0·1	9·9	65·2	73·1	76·6	76·6
Light orange . 4	0	0	0	0	0·4	32·7	76·6	78·3	78·3	78·3
Green 5	0	0	0	0	25·9	36·6	3·7	0·5	0·1	0
Blue-green . . 6	0	0·1	35·0	48·3	48·3	32·7	5·8	0·4	0·	0
Blue 7	0	0	17·5	29·1	0·1	0	0	0	3·7	1·3
Purple . . . 8	0	23·1	29·1	0	0	0	0·1	1·8	13·0	60·8
Daylight . . . 9	0	65·2	87·9	82·0	73·1	58·1	44·0	36·6	38·4	36·6
Light neutral . 11	0	9·2	46·1	16·4	23·1	23·1	23·1	20·6	36·6	46·1
Orthochromatic . 12	0	0	0·1	9·2	46·1	58·1	46·1	36·6	46·1	58·1
Ultra-violet . . 14	4·6	73·1	0·1	0	0	0	0·3	2·9	9·2	23·1
Crookes A. . . .	0	10	82	86	90	90	82	92	91	90
Crown 1·51 Nd. . .	20	54	92	92	92	92	92	92	92	92
Yellow noviol B. .	0	0	0	0	85	88	86	86	85	85
Dark amber „ . .	0	0	2	10	37	57	64	67	70	71
Blue-green . . .	0	3	35	37	56	70	68	65	65	—
Cobalt blue AA . .	0	60	75	55	7	0	0	0	30	60
Selenium ruby . .	—	—	—	—	0	2	8	80	80	80
Gold ruby . . .	—	—	—	5·0	1·0	0·2	33	64	70	73
Copper ruby . . .	—	—	—	—	7·0	5·0	44	68	72	74
"*Calorex*" . . .	0	0	22	40	68	64	60	40	20	7
Special welders' glass	0	10	35	8	4	5	6	5	8	10
„ „ „	0	0	17	40	50	20	1	0	1	3
Willson weld, shade 3	0	1	1	2	15	30	25	20	7	—
Novi weld, No. 3 .	0	1	1	2	7	18	23	20	13	—

B. VISUAL TRANSMISSION—GEHLHOFF AND THOMAS GLASSES.

Oxide.	Colour.	Thickness, mm.	Transmission %. λ (mμ).								
			350.	400.	450.	500.	550.	600.	650.	700.	750.
Mn_2O_3 0·1% . . .	—	2·0	—	—	94	90	90	90	90	90	92
„ 1·0% . . .	—	2·0	—	—	50	38	46	56	60	62	62
„ 5·0% . . .	—	2·0	—	—	8	1	5	13	21	31	53
CoO 0·1% . . .	Blue.	2·0	—	—	87	56	42	28	28	67	76
„ 1·0% . . .	Purple.	2·0	—	—	67	6	0	0	0	17	61
NiO 0·5% . . .	—	2·0	—	—	40	20	17	21	16	48	64
„ 1·0% . . .	—	2·0	—	—	17	4	3	5	3	31	55
CuO 0·5% . . .	Green.	2·0	—	—	94	92	84	82	76	75	80
„ 4·0% . . .	Blue-green.	2·0	—	—	85	74	47	16	5	2	1
Cr_2O_3 0·2% . . .	Yellow.	2·0	—	—	40	78	86	76	68	74	85
„ 0·8% . . .	—	2·0	—	—	0	45	75	50	33	40	65
U_3O_8 1·0% . . .	—	2·0	—	—	78	85	85	86	86	87	88
„ 16·0% . . .	—	2·0	—	—	15	35	73	77	86	84	86
Fe_2O_3 0·05% . . .	—	—	56	68	78	90	94	86	72	—	—
0·18% . . .	Green.	—	30	50	61	82	74	57	43	—	—

TABLE VI.

A. ULTRA-VIOLET TRANSMISSION OF COMMERCIAL ULTRA-VIOLET TRANSMITTING GLASSES, 2·0 MM. THICKNESS.

	Transmission %. λ ($m\mu$).								
	260.	270.	275.	285.	294.	302.	312.	334.	340.
"*Brevos*"	0·5	4·5	9·5	34·8	56·5	67·5	78	89	92
"*Ultravit*"	0·6	4·5	9·5	31·0	54·0	65	75	88·5	91
"*Uviol*"	0·5	4·5	10·0	35·0	59·0	73	82·5	90	91
"*Sanalux*"	0·8	5·0	10·0	35·1	50	77·5	74·0	88	91
"*Vita*"	1·0	6·0	12·5	34·9	50	61	72·5	88	91
"*Helioglass*"	0	1·0	10	25	48	56	73	86	88
Belgian window	0	0	0	0	0	0	52	58·4	80

B. ULTRA-VIOLET TRANSMISSION, SCHOTT OPTICAL GLASSES, 2·0 MM. THICKNESS.

	n_D.	Transmission %. λ ($m\mu$).						
		289.	303.	313.	334.	366.	405.	436.
Borosilicate crown	1·5106	25·8	57·1	75·8	89·0	91·7	91·8	91·8
Crown	1·5124	21	54·3	74·0	88·8	91·6	92	92
Barium crown	1·5413	0	42·4	64·7	87·0	91·7	91·8	91·7
Light barium flint	1·5506	0	33	66·2	87·2	91·5	91·8	92
Light flint	1·5810	0	4·1	39·8	80·3	90·3	91·2	91·5
Flint	1·6204	0	0	21	77·3	90·6	91·9	91·7

C. SOLARISATION EFFECT—COMMERCIAL ULTRA-VIOLET TRANSMITTING GLASSES.

	Thickness in mm.	Transmission % for $\lambda = 302$ $m\mu$.		
		Initially.	1 month exposure to sun.	10 hours exposure to Hg. lamp.
"*Vita*"	2·01	51·9	26·5	21·8
"*Helioglass*"	2·00	58·0	46·2	36·7
"*Ultravit*"	2·05	62·3	47·0	37·6
"*Holviglass*"	2·40	41·1	37·4	33·2
"*Sanalux*"	2·14	51·0	29·0	21·2
Ultra-Violet glass . . .	2·07	52·8	48·9	41·0
"*Sunlit*".	1·92	65·0	46·0	38·2
"*Neuglas E.*"	2·30	61·7	58·7	51·0
"*Uviol Jena II*" . . .	1·97	49·5	43·8	30·1
"*Corex*"	2·01	81·3	78·7	70·1

Loss by Reflection at the Glass–Air Surface and Means of Reducing it.—According to Fresnel's law the loss of light by reflection at an air–glass surface is related to the refractive index *n* of the glass by the expression $\left(\frac{n-1}{n+1}\right)^2$ and for a soda-lime–silica glass of refractive index approximately 1·5 this loss is 4%, or much more than that lost by actual absorption in most optical systems whilst for a lead glass it is much greater. H. D. Taylor ("Adjustment and Testing of Telescope Objectives," York, 1896) noted that weathered photographic lenses were much faster than freshly polished areas and suggested treatment of new lenses by weathering agents, *e.g.* H_2S or alkali sulphide solutions to produce thin films on the surfaces. F. Kollmorgen (Trans. Illum. Eng. Soc. New York, 1916, **2**, 220) reported a considerable reduction of reflection loss by surface treatment of lead flint or barium crown glasses, and F. E. Wright with J. B. Ferguson described similar tests with 1% acid sodium phosphate or copper sulphate solutions, amongst others, for 18 hours at 80° (Manufacture of Optical Glass and Optical Systems, U.S. Ordnance Dept. Document No. 2037, 1921, p. 77). Work by J. Strong (J. Opt. Soc. Amer. 1936, **26**, 73), K. B. Blodgett (Physical Rev. 1939, **55**, 391),

TABLE VII.—INFRA-RED TRANSMISSIONS.

	Min. thick.	Transmission %. λ (μ).							
		0·5.	1·0.	1·5.	2·0.	2·5.	3·0.	4·0.	5·0.
Selenium ruby . . .	5·9	0	60	65	70	30	2	0	0
Copper ruby	2·5	0	80	83	87	60	40	38	0
Yellow green	3·4	—	3	30	70	35	20	5	0
Novi weld, shade 4½ . .	—	17	0	2	4	12	5	5	0
Crookes	1·98	45	0	2	4	10	6	12	0
"*Calorex*"	2·0	68	1	8	13	8	3	0	0
82 SiO_2 18 NaO_2 . .	2·0	—	94	94	93	76	60	48	3
64 SiO_2 18 MgO 18 Na_2O . .	2·0	—	82	85	88	71	60	65	9
42 SiO_2 40 ZnO 18 Na_2O . .	2·0	—	82	82	82	75	69	71	15
78 SiO_2 4 NiO 18 Na_2O . .	2·0	—	10	20	10	16	21	32	4
78 SiO_2 4 CoO 18 Na_2O . .	2·0	—	50	20	0	10	27	43	4
70 SiO_2 12 CuO 18 NaO . .	2·0	—	0	15	48	62	70	60	6
Crookes A	2·0	90	90	—	89	—	39	27	0
Crookes No. 246 . . .	2·0	0	1	—	5	—	9	—	—
Fieuzal	2·0	40	76	—	82	—	29·5	25	3
Crown glass	2·0	92	91	—	90	—	45	18	0

C. H. Cartwright and A. F. Turner (*ibid.* 1940, **55**, 675A) and F. L. Jones and H. J. Horner (J. Opt. Soc. Amer. 1941, **31**, 34) has shown that the effect is a function both of the nature of the layer left upon the surface and upon its thickness, being due to interference phenomena. There is for a surface layer of given refractive index an optimum film thickness that produces minimum loss by reflection, and the lower the refractive index of the film the better the effect. Blodgett worked with insoluble metallic soap films, *e.g.* barium stearate and cadmium arachidate, whilst other workers either produced weathered films by dilute acid attack (Jones and Horner), which behaved optically as if of silica, or deposited, by evaporation *in vacuo*, thin films of minerals of low refractive index such as fluor spar. Jones and Horner state that if after filming by 1% nitric acid the washed specimen is heated to a temperature just short of deformation, the film becomes quite durable to the handling ordinarily given to optical components. By treatments such as the above the transmission of simple lenses for white light has been raised to 99% and over.

Electrical Conductivity.—It is agreed by most investigators that conductivity in

$$Na_2O—CaO—SiO_2$$

glasses is due to the **Na** ion, though H. H. Poole (Nature, 1921, **107**, 584) questions its purely electrolytic nature. More systematic work, particularly on alkali-free glasses, is needed to extend our knowledge (Morey). E. Warburg and T. Ihmori (Ann. Phys. Chem. 1886, [iii], **27**, 481) showed that the absorbed surface film on glass can conduct to a large extent, and precautions must be taken to eliminate this in determination of the "bulk conductivity," *e.g.* by working *in vacuo*. According to M. Fulda (Sprechsaal, 1927, **60**, 769 *et seq.*) surface resistivity at 25° at 100% humidity of the glass 18% Na_2O 82% SiO_2 was raised by substituting Al_2O_3, B_2O_3, BaO, Fe_2O_3, CaO, PbO, ZnO, or MgO for SiO_2. In all cases a maximum value was reached. Of these the most effective was CaO (at approximately 8%), then B_2O_3 (20%), BaO (10%), Al_2O_3 (15%), Fe_2O_3 (18%), MgO (12%), ZnO (13%), PbO (25%). A. Gray and J. J. Dobbie (Proc. Roy. Soc. London, 1898, **63**, 38; 1900, **67**, 197) gave data for electrical resistance of glasses of known composition. Fulda (*l.c.*) working on the 18 Na_2O, 82 (SiO_2+RO) series of Gehlhoff and Thomas showed that CaO increased specific resistivity most (up to 30% additions), then BaO, B_2O_3, MgO, PbO, ZnO, the last named having very little affect, whilst Al_2O_3 caused a reduction. In the alkali silicate glasses, soda reduced resistivity more than potash weight for weight when replacing silica. For data on commercial glasses and porcelains, *see* E. Seddon, W. J. Mitchell and W. E. S. Turner, J. Soc. Glass Tech. 1939, **23**, 197. The only systematic work of high accuracy is that by E. Seddon, E. J. Tippett and W. S. S. Turner (*ibid.* 1932, **16**, 450) on the soda-silica glasses.

Temperature Effect.—Specific resistivity decreases rapidly with temperature, falling from around 10^{14} ohms to about 10^4 at the annealing temperature and to about unity in the region of the melting temperature, so that once heated glass can be electrically melted by passing a current through the mass. There are sharp breaks in the resistance–temperature curves at

T_g, and the effect of strain on resistance is very marked. Pyrex resistant glass has a surface resistivity of 10^{14} ohms at 34% humidity, 5×10^8 ohms at 84% and a volume resistivity of 10^{14} ohm c.c. E. Balle (cited by F. Eckert Jahresber. Radioakt. Elektronik, 1923, **20**, 93, 190) quotes the following values of conductivity κ in 10^{12} ohm^{-1} cm.$^{-1}$:

SiO_2	70·4	69·0	62·6	56·2	67·7	48·1	51·7
B_3O_3	7·4	2·5	—	—	8·0	4·5	—
Na_2O	5·3	4·0	4·5	1·5	10·0	1·0	1·5
K_2O.	14·5	16·0	8·5	11·0	—	7·5	9·5
CaO	2·0	8·0	—	—	—	—	—
BaO	—	—	—	15·0	—	28·3	20·0
ZnO	—	—	—	9·0	9·0	10·1	7·0
PbO	—	—	24·1	7·0	—	—	10·0
κ at							
100°	0·012	0·0132	0·00542	0·019	0·0025	0·00256	0·00233
125°	0·0703	0·0672	0·0418	0·0416	0·015	0·0134	0·00994
150°	0·334	0·425	0·221	0·0968	0·0684	0·0406	0·039
175°	1·59	2·32	1·57	0·5076	0·668	0·106	0·116
200°	6·9	—	7·69	2·38	2·544	0·374	0·393

Dielectric Properties.—*Dielectric Constant* or Specific Inductive Capacity κ varies between 3·7 and 16·5. Increase of temperature increases κ (rise of 120° changes value by 3–14%). Values vary with the frequency of the current applied. For low frequencies the limit of stability is about 80° for lime glasses and 120° for borosilicate, while at 10^4 cycles the corresponding values are 140° and 240° respectively. Values of κ are white plate 7·1, ordinary flint (lead) 7·4, densest silicate flint 16·1, Uviol crown 5·6, fluorcrown 5·8, dense flint 10·0, fused silica 3·7, Pyrex glass 4·1–5·0.

Dielectric Loss $= \kappa \times \delta$ (δ, phase difference angle $= 90° -$ phase angle θ) and $P = VI \sin \delta$. Values vary with frequency, *e.g.* Pyrex glass at 1,000 cycles has $\kappa\delta \times 10^4 = 400$, at 100,000 the value is 371, at 500,000 is 330, at 10^6 is 190. For Corning 707 glass, values are smaller still, ranging from 22–70 according to frequency, whilst those for other glasses range up to 2,000 though most lie around 100–200.

Dielectric Strength or resistance to puncture by electric discharge between opposite faces is given by the relation $V = ad + \beta$ where V is the breakdown voltage in kilovolts, d the thickness in cm. and a and β are constants. It is difficult to draw conclusions as to the effect of composition. P. H. Moon and A. S. Norcross (J. Amer. Inst. Elect. Eng. 1930, **49**, 125) reported strengths of 3,100 kv. for lead glass irrespective of thickness (0·04–0·28 mm.) and from 300 kv. at 0·04 mm. to 1,000 kv. at 0·28 mm. thickness for lime glass.

Elastic Properties.—The behaviour of optically worked glass articles on standing (*see* C. Pulfrich, Hovestadt's "Jena Glass," Everetts' translation, 1902; F. E. Wright, "The Manufacture of Optical Glass and Optical Systems," Government Printing Office, Washington, D.C. 1921) indicates that flow may occur in glass at ordinary temperatures so that glass does not possess a true elastic limit but behaves rather as a very viscous fluid even at these temperatures. E. W. Washburn, G. R. Shelton and E. E. Libman (Univ. Illinois Bull. 1924, **140**, 48) support this view. The properties have been studied by Winkelmann and Schott (Ann. Phys. Chem. 1894, [iii], **51**, 697; 1897, [iii], **61**, 105); R. Straubel (*ibid.* 1899, [iii], **68**, 369), J. R. Clarke and W. E. S. Turner (J. Soc. Glass Tech. 1919, **3**, 260), H. T. Jessop (Phil. Mag. 1921, [6], **42**, 551) and G. Gehlhoff and M. Thomas (Z. tech. Physik, 1926, **7**, 105). Several workers, including Winkelmann and Schott, and Gehlhoff and Thomas, did not analyse the glasses, an omission which detracts from the value of the results, and the factors of Winkelmann and Schott must be regarded with suspicion.

Young's Modulus (E) of fused silica was given as 700 kilobars (1 kilobar $= 10^9$ dynes per sq. cm. $=$ 1,020 kg. per sq. cm.) by R. B. Sosman ("Properties of Silica," p. 437, 1927). Clarke and Turner found for the soda-lime–silica glasses having an SiO_2 content of 74–75% that increase of lime at the expense of soda raised E from 567 kilobars when only 0·2% CaO was present, to 711 kilobars when the glass contained 10·4% CaO. The results were expressed in the form $E = 13·9\,(\%CaO) + 565·6$. Gehlhoff and Thomas (*l.c.*) working on their series of glasses found that in the two-component glasses increase of Na_2O or K_2O at the expense of SiO_2 decreased E, K_2O more so than Na_2O. In the three-component glasses, PbO had very little effect whilst that of BaO and ZnO was not large and became constant after about 20% and 25% addition respectively at values of 690 and 700 kilobars respectively. CaO had a marked effect, raising the value from 600 to about 900 kilobars for a 10% addition and pro rata; B_2O_3 increased the value not quite so much as CaO up to 15–20% ($E = 900$), and then caused a falling off. Fe_2O_3 caused a steady but less increase in E up to 30% addition (750 kilobars) and Al_2O_3 only raised the value to 660 for a 20% addition. W. Horak and D. E. Sharp (J. Amer. Ceram. Soc. 1935, **18**, 282) found that in glasses containing SiO_2 74, Na_2O 17% with 9–0, 8–1, 7–2 and 5 CaO—4 ZrO_2 respectively, the corresponding values of E were 439, 367, 325, 275 kilobars. Clarke and Turner found discrepancies amounting to 28% when they applied Winkelmann and Schott's factors to their experimental results. For more complex glasses, A. A. Griffith (Trans. Roy. Soc. London, 1920, A, **221**, 163) found $E = 621$ kilobars, Poisson's ratio (σ) $= 0·251$ for SiO_2 69·2, Na_2O 0·9,

K_2O 12·0, CaO 4·5, Al_2O_3 11·8, MnO 0·9%; F. Twyman and J. W. Perry (Proc. Physical Soc. 1922, **34**, 151) found E=619·8 and σ=0·196 for SiO_2 54·8, PbO 34·6, Na_2O 6·12, K_2O 4·3%; G. Berndt (Z. Instrumentenk. 1920, **40**, 20) found E=798·9 for a borosilicate crown SiO_2 69·6, B_2O_3 9·9, BaO 2·5, Na_2O 8·4, K_2O 8·4%; F. D. Adams and E. G. Coker (Carnegie Inst. Wash. 1906, Pub. No. 46) gave 723·9 for plate glass and A. E. Williams (J. Amer. Ceram. Soc. 1923, **6**, 980) for single and double strength window glass E=760, for 29–39 oz. clear sheet 725, polished plate 690, and rough rolled plate 670 kilobars. Increase of temperature usually causes decrease of E. A. E. Badger and W. B. Silverman (*ibid.* 1935, **18**, 276) found a fall of 658–560 kilobars from 25° to 450°C. for the glass SiO_2 68·1, Na_2O+K_2O 18·6, MgO 4·1, CaO 5·8, $Al_2O_3+Fe_2O_3$ 3·4%, the change being slow to 250° (E=659·3–0·125*t*) then more rapid between 350–450° (E=639–0·18*t*). E. Wandersleb (Ann. Physik. 1902, [iv], **8**, 367) found for borosilicate glasses containing Sb_2O_3 that E increased with temperature, though silicate glasses with up to 15% Sb_2O_3 showed a decrease, and J. M. Ide (J. Geol. 1937, **45**, 689) found increases for fused SiO_2 and Pyrex glasses (722 and 630 at 0°, to 763 and 673 at 400° respectively).

Strain produces values smaller than for properly annealed glass. G. Berndt (*l.c.*) found E=755 and 814 for strained and annealed specimens of a borosilicate crown, and J. Meikle (J. Soc. Glass Tech. 1933, **17**, 419) found 780 and 759 for $\frac{1}{4}$ and $\frac{5}{16}$ in. toughened glass, the untreated (commercially annealed) glass having the values 869 and 863 kilobars.

Compressibility (β) is the reciprocal of the bulk modulus and is given as the relative volume change per kilobar pressure. Adams and Williamson (J. Franklin Inst. 1923, **195**, 475) found for plate glass SiO_2 73, CaO 12, Na_2O 15%, at pressures up to 12 kilobars that $\beta=2{\cdot}27$, 2·23 and $2{\cdot}05\times10^{-3}$ respectively at pressures of 0, 2 and 10 kilobars. A basalt glass gave $\beta=1{\cdot}45\times10^{-3}$ kilobars^{-1} between 2 and 12 kilobars. P. W. Bridgman (Amer. J. Sci. 1925, **10**, 359) found for Pyrex glass that β increased with pressure, and L. H. Adams and R. E. Gibson (J. Wash. Acad. Sci. 1931, **21**, 381) gave $10^6\beta=304{\cdot}5+1{\cdot}42P$ (P in kilobars), and for silica glass, which had the largest increase of any substance measured, $10^6\beta=2{,}689+15$ P. F. Birch and R. B. Dow (Bull. Geol. Soc. Amer. 1936, **47**, 1235; J. Appl. Physics, 1937, **8**, 129) state that a negative coefficient of compressibility is possible only below a temperature depending on glass composition, ranging from about 220° for lead glass to above 400° for silica glass, the value for Pyrex glass being 270°.

Poisson's Ratio (σ) varies from 0·271 for a dense barium crown glass to 0·197 for a borosilicate glass and for ordinary glasses is about 0·22. For silica glass it is 0·14, for medium flint, 0·196.

After-working Effect (*a*) *Elastic.*—When subjected to stress for some time, all the strain does not immediately disappear from glass on removal of the stress. G. Weidmann (Ann. Phys. Chem. 1886, [iii], **29**, 241), showed the effect was determined by the duration of loading and the glass composition, and defined the elastic after-effect as the ratio of deformation remaining after a given time to the original deformation. Values of this ratio for Jena 16^{III} and a Thuringian glass were for removal of load after 20, 90 and 180 seconds, 0·0065, 0·0106; 0·0025, 0·0075; 0·0014, 0·0057 respectively. *See also* K. H. Borchard (Sprechsaal 1934, **67**, 297), and F. W. Preston, quoting C. D. Spencer (J. Amer. Ceram. Soc. 1935, **18**, 220).

(*b*) *Thermal.*—The change of zero with time of a thermometer is well known (*see* Hovestadt's "Jena Glass," Everetts' translation, 1902). Thermometer glasses containing both Na_2O and K_2O, not one alone, were found by H. F. W. Wiebe and O. Schott (Z. Instrumentenk. 1886, **6**, 167) to be worst in this respect, and Weidmann (*l.c.*) showed that a thermally good glass was also good elastically. The standard thermometer glasses have, according to E. F. Mueller (Int. Critical Tables, 1926, **1**, 55), the following depression constants [1] (°C.) Verre dur 0·07–0·11, Kew glass 0·20, Jena 16^{III} (Corning 881) 0·04–0·08, Jena 59^{III} (Corning 880) 0·03–0·04, Jena 1565^{III} 0·01, Jena combustion 0·03.

Strength of Glass.—Tests give results lower than those deduced on theoretical grounds. Reduction of size of test piece, *e.g.* using fine threads for tensile tests, gives much increased values, from which most workers deduce that the ruling factor is the surface flow (A. A. Griffith, Trans. Roy. Soc. London, 1920, A, **221**, 162; J. T. Littleton, Physical Rev. 1923 (2), **22**, 510; F. W. Preston, J. Soc. Glass Tech. 1933, **17**, 4). Preston (*ibid.* 1926, **10**, 234; J. Amer. Ceram. Soc. 1926, **9**, 654; 1931, **14**, 419; *also* with J. T. Littleton, J. Soc. Glass Tech. 1929, **13**, 336) studied the fracture of glass and showed that the faster the rate of travel of a fracture the more roughly "hackled" was the broken surface, and the slower the travel the more polished and smooth was the surface.

Gehlhoff and Thomas (*l.c.*) found that the oxides they studied improved the tensile strength in their series of glasses in the order (descending) CaO, B_2O_3 (up to 15% then decreased strength), BaO, Al_2O_3, PbO, SiO_2, MgO and ZnO were without effect, and Fe_2O_3 gave reduced strength. For bending strength they found improvement, in descending order, from CaO (up to 16% and then a falling off), BaO (up to 20%) PbO (up to 20%), ZnO (up to 10%), Fe_2O_3, MgO, B_2O_3 (up to 17%), whilst Al_2O_3 gave reduced strength. CaO, BaO, PbO, B_2O_3 and Fe_2O_3 gave reduced crushing strength, MgO and ZnO had no effect and Al_2O_3 gave increased strength. Actual strength values for various glasses range from 0·52 to 0·83 kilobars (1 bar=1·02 kg. per sq. cm.) according to Winkelmann and Schott (Hovestadt's "Jena Glass," Everetts' translation), or 0·54 to 0·92 kilobars according to A. Lecrenier (Le Verre, 1924, **4**, 149) for tensile strength, the corresponding values for compressive strength being 5·9 to 12·4 (W. and S.) and 7·6–9·1 kilobars (Lecrenier, *l.c.*). The values are not easy to determine, and the spread of results is generally large. The approximate tensile strength of plate glass is 0·87 kilobars. Silica glass, according to R. Sosman ("Properties of Silica, 1927"), has values of 3–8 kilobars for tensile, and 19·5 kilobars for compressive, strength.

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[1] The depression constant is the lowering of the zero produced by heating to 100° and cooling quickly.

The effect of various factors on the strength of sheet glass may be summarised as follows: *Nature of Surface.*—Ordinary sheet according to A. E. Williams (*l.c.*) has a modulus of rupture in lb. per sq. in. of 6,111–12,755, rough cast plate 5,500–8,625, polished plate 6,027–6,997, wired rough cast 5,640–7,900, wired polished 5,569–7,470 using specimens 18 × 2 in. (though O. Graf, Glastech. Ber. 1925, **3**, 153, found wired glass less strong than similar glass without reinforcement). *Method of Support.*—O. Graf gave for 20 × 20 cm. test pieces of polished plate, ordinary sheet, wired, figured rolled and plain rolled specimens the values 7,250, 8,960, 5,410, 5,410, 4,830 when supported on opposite sides, and 7,680, 18,640, 6,260, 8,110, 5,840 when supported on all four sides. *Duration of Loading.*—For a uniform (hydraulic) pressure test Graf gave values 4,600–8,600 for instantaneous breaking strength, and 3,300–4,600 for the strength under continued load (duration varying from 0·03–108 hours). A. J. Holland and W. E. S. Turner (J. Soc. Glass Tech. 1940, **24**, 46) found for a centre-loaded beam test that the mean time to cause fracture of small specimens 10 × 0·08 × (0·265–0·285) cm. cut from sheet glass varied with the load as follows: for 100% of mean breaking load, 34 seconds; 90%, 97 seconds; 80%, 6 minutes 4 seconds; 70%, 90 minutes; 60%,[1] 16 hours 14 minutes; 50%,[1] 39 hours 40 minutes; 40%,[1] 33 hours 50 minutes. They tested 100 specimens in each category. *Width of specimen* and *nature of finish of cut edges.*—Holland and Turner (*ibid.* 1934, **18**, 225; 1936, **20**, 72; 1937, **21**, 383) illustrate the influence of these factors by the following table:

Width (cm.).	Cut and lower edge in tension.* Modulus (kg. per sq. cm.).	Edges ground and polished.		Edges ground and fire-polished.	
		Width (cm.).	Modulus (kg. per sq. cm.).	Width (cm.).	Modulus (kg. per sq. cm.).
0·6–0·7	603	0·395	646	0·4	1·299
0·7–0·8	576	0·475	620	0·485	1,274
0·8–0·9	564	0·725	584	0·73	1,114
0·9–1·0	546	0·730	553	0·775	1,030
1·0–1·1	534	0·805	579	0·945	991
1·1–1·2	533	0·975	549	1·19	935
1·2–1·3	500	1·17	531	—	—
1·3–1·4	498	—	—	—	—
1·4–1·5	494	—	—	—	—

* Lower and more reproducible values obtained than when cut edge is uppermost and in compression.

Span under Load.—Data from the Building Research Station show a fall from 9,500 lb. per sq. in. to 7,900, 7,800, 7,750, 7,750, as the span under test increased from 0·7 in. to 10, 20, 30 and 40 in.

Impact Strength may be measured by the work in inch-ounces or g.-cm., etc., of a ball falling on the test piece, by the force of the blow of a swinging pendulum (or, rarely, the energy absorbed in the impact) or by height of fall of a given weight on to a ram in the hydraulic shock test. Using the pendulum method F. W. Preston (J. Amer. Ceram. Soc. 1931, **14**, 428) has recalculated the data of A. E. Williams (*l.c.*) and gives the impact strength (f_i) as:

$$\sqrt{\frac{18\,\text{E (Young's Modulus in lb. per sq. in.)} \times \text{F (ft. lb. to fracture)}}{l \times b \times \text{thickness (all in inches)}}}$$

the values being as below:

Type.	f_i (average) lb. per sq. in.	Average modulus of rupture, F.	Ratio f_i/F.
Sheet single strength	12,060	8,270	1·46
,, double ,,	11,250	7,880	1·43
,, 26 oz. . . .	10,870	7,460	1·46
,, 34 oz. . . .	10,460	7,230	1·45
,, 39 oz. . . .	10,540	6,980	1·51
Polished plate, ¼ in. .	8,970	6,030	1·49
Rough cast, ¼ in. .	9,770	7,730	1·26
,, ,, ⅜ in. .	9,440	7,500	1·26
Plain rolled, ¼ in. .	8,060	5,150	1·67
Wired, ¼ in. . . .	8,090	5,570	1·45

In the falling ball test, specimens of ¼ in. and $\frac{5}{16}$ in. thick of ordinary plate glass 14 in. × 10 in. break at 16·7 and 23·1 in. drop of a 0·5 lb. steel ball or 14·5 and 19 in. drop of a 1·68 lb. ball, whilst toughened ("Armourplate") glass of similar dimensions breaks at 129 and 160 in. drop of the 0·5 lb. ball when simply supported on two rods 12 in. apart. The strength of glass fibres was found by A. A. Griffith (*l.c.*) to increase from 1·715 kilobars per sq. mm. for 1·016 mm. diameter to 2·912 for 0·1067 mm., 5·48 for 0·0508 mm., 12·72 for 0·0152 mm. and 33·83 for

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[1] Mean time calculated from specimens that broke. The proportion of specimens unbroken after 1,000 hours increased from 0 at 70% load to all at 30% load

0·0033 mm. F. O. Anderegg (Ind. Eng. Chem. 1939, **31**, 290) found the tensile strength T of fibres (in lb. per sq. in.) was related to diameter d (in 0·0001 cm.) by the equation:

$$T = 20{,}000 + \frac{550{,}000}{d+0{\cdot}2} + \frac{600{,}000}{(d+0{\cdot}2)^2}$$

CLASSIFICATION OF GLASSES.

As almost all glasses contain silica, and, moreover, certain metallic oxides such as calcium oxide and sodium oxide, are present in many different types of glass, a simple classification based on composition is not available, and it is usual to classify glasses according to their use:

(1) Lime–Soda Glasses for Common Use.—This type of glass is the most important, since bottles of all kinds, window glass and plate glass are made from it, as well as many articles for domestic use such as the cheaper forms of tumblers and pressed table glassware.

A. *Common Bottles and Glass Containers.*—Analyses of actual samples show that considerable diversity of composition exists.

A.	1.	2.	3.	4.	5.	6.
SiO_2	75·34	73·06	74·0	73·26	65·20	61·90
B_2O_3	—	—	0·4	—	—	—
Al_2O_3	0·45	1·30	0·5	1·31	3·52	4·44
Fe_2O_3	0·30	0·30	0·06	0·09	2·20	1·66
CaO	6·83	8·70	8·5	7·24	9·48	17·95
MgO	0·21	0·17	0·2	0·17	0·12	6·38
Na_2O	13·78	15·26	16·0	17·88	16·05	6·16
K_2O	3·41	0·98	—	—	—	1·13
As_2O_3	(Sb_2O_3 tr.)	—	trace	trace	(MnO 3·08)	—
Se	—	—	trace	trace	-	—
CoO	—	—	trace	trace	—	—

1. Continental-made soda-water siphon.
2. Pressed meat jar (pale green).
3. Modern colourless automatic-machine-made container (good durability).
4. Old type colourless automatic-machine-made bottle (poor durability).
5. Modern dark green beer bottle made on automatic feeder-fed machine.
6. Champagne hand-made wine bottle (continental).

B. *Pressed Glassware* of the cheaper types frequently has a composition somewhat similar to the bottle glass A 4.

A considerable improvement in the appearance of pressed table-ware may be obtained by replacing the calcium partly by barium oxide, and the latter is accordingly frequently used.

C. *Window and Plate Glass* from different sources do not vary greatly in composition, as illustrated by the figures given in the table at the top of the next column.

	Window glass.		Plate glass.	
	Old French mouth-blown.	Modern British and American.	American (Ford) for automobiles.	British.
SiO_2	71·6	72·5–73·0	72·0	72·0
Al_2O_3	0·5	0·4–1·8	0·8	0·5
Fe_2O_3		0·08–0·10		
CaO	15·5	8·5–9·0	11·6	9·5
MgO	—	2·5–3·0		3 3
Na_2O	12·2	13·0–14·5	15·3	14·0
K_2O	—	0–0·4	—	—

D. *Illuminating Glassware.*—A good deal of the common illuminating ware such as lamp chimneys and globes and shades is made from a calcium–sodium or calcium–sodium–potassium glass, with or without other oxides. Calcium–sodium glass containing magnesium has come into extended use for the manufacture of electric light bulbs, replacing the more expensive lead glass. Common machine-made globes have a composition not much different from that given for the bottle glass A 4. Other calcium-containing glasses for illuminating purposes are included for convenience in the section on illuminating glassware.

(2) Lead-Containing Glasses.—The best British glass for tableware, known as English crystal, or heavy crystal glass, contains silica, lead oxide and potash, the proportion of lead oxide in the finished glass exceeding 30%.

Lead oxide has, until a few years ago, been an important oxide in the composition of glass for electric light bulbs, the amount present varying from 18 to 30%. Other illuminating ware, especially in opal glass, usually has a lead oxide base. Glass rod and tubing intended for use in the manufacture of electric light bulbs has also hitherto contained lead oxide.

As examples of lead-containing glasses, the following analytical compositions of commercial bulbs may be given:

	British rod for electric lamps.	English full crystal table-ware.	German "lead crystal."	Demi-crystal (foreign).	
SiO_2	62·85	53·1	63·14	62·88	70·9
B_2O_3	—	—	—	—	2·0
PbO	21·48	35·1	21·71	19·84	8·8
Al_2O_3	0·35	0·15	0·10	0·29	0·4
Fe_2O_3	0·10	0·022	0·008	0·014	0·1
CaO	0·40	—	—	0·76	3·8
MgO	0·10	—	—	—	—
BaO	—	—	—	0·68	2·6
ZnO	0·93	—	—	—	—
Na_2O	9·00	—	2·02	1·63	—
K_2O	4·60	11·4	12·88	12·83	11·5

(3) Chemical, General Scientific and Heat-Resisting Glassware may be of very widely different composition, which may be simple, such as in the case of Pyrex glass, the chief constituents of which are silica and boric oxide, or may be complex like the British chemical-resistant glasses, containing silica, boric oxide, calcium, magnesium, aluminium and sodium oxides with zinc oxide also in many cases.

A. *Chemical Glassware.*—The table given at the top of the next page states the percentage composition of some different types.

	Jena "Duran."	"Resista."	Pyrex.	Moncrieff (1926).	Chance Bros. (1924).	Wood Bros. (1926).	Jena (1920).	British present day types.		
								1.	2.	3.
SiO_2	76·1	75·3	80·6	75·3	71·2	59·3	74·5	79–80·5	66·5	76·7
B_2O_3	16·0	15·8	11·9	11·3	12·0	9·6	4·6	12–13	10·9	11·2
Al_2O_3. . . .	1·75	2·5	2·0	3·0	3·5	7·6	8·5	2–2·75	3·9	2·4
Fe_2O_3 . . .	N.D.	N.D.	0·14	N.D.	0·1	N.D.	—	—	—	—
ZnO	—	—	—	2·8	—	5·2	—	—	6·2	2·4
(BaO) . . .	—	—	—	—	—	—	3·9	—	—	—
CaO	0·2	0·7	0·2	0·5	1·3	5·0	0·8	0·2	2·4	0·4
MgO	—	—	0·3	—	—	1·7	0·1	trace	trace	trace
Na_2O. . . .	5·4	4·4	3·8	6·5	8·6	8·8	7·7	3	6·8	4·8
K_2O	0·6	1·1	0·6		—	2·9	—	0–0·5	1·2	1·5
Sb_2O_3 . . .	—	1·3	—	—	3·4	—	—	—	—	—
As_2O_3 . . .	—	—	0·7	—	—	—	—	0–0·5	0·2	0·1
Approx. coef. of linear thermal expansion $a \times 10^8$	—	—	—	—	—	—	—	320–330	504	440

B. *Lampworking Glass*, from which light blown articles of glassware (condensers, absorption bulbs, pipettes, etc.) are made, may also vary considerably in percentage composition as indicated in the following table:

PERCENTAGE COMPOSITION OF GLASSES FOR LAMP BLOWN APPARATUS.

	British glasses (1937–38).						Jena thermometer glasses.	
	"Lead" glass.	"Soft soda" glasses.			Harder glasses.			
					Amber.	Resistant glasses.	59III.	16III.
SiO_2 . .	56·6	69·4	68·2	70·5	69·4	"*Pyrex*,"	72·86	66·58
Al_2O_3 . .	0·8	3·8	4·0	1·6	1·8	"*Monax*,"	6·24	3·84
B_2O_3 . .	0·2	—	0·7	—	3·4	"*Hysil*,"	10·43	0·91
PbO . .	30·2	—	—	—	—	Wood	—	ZnO 6·24
CaO . .	—	6·4	5·5	6·8	9·2	and	0·35	7·18
MgO . .	—	—	2·2	3·5	2·2	others.	0·20	0·17
Na_2O . .	5·1	13·8	17·0	16·9	8·2		9·82	14·80
K_2O. . .	7·2	6·5	2·2	0·7	—		0·10	trace
Fe_2O_3 . .	—	—	—	—	2·3		—	—
Mn_3O_4 . .	—	—	—	—	3·1		—	—

Some very soft glasses serving as seals on intermediate joints in lampworking operations are made either from lead oxide or with a considerable proportion of boric oxide. Others contain zinc oxide and boric oxide, these being fused with common soft soda–lime glass to form a soft sealing-in glass.

C. *Heat-Resisting Glass.*—Glass made for the purpose of resisting chemical action is also heat resisting. Thus, Jena heat-resisting lamp chimneys had a composition similar to the Jena chemical glassware, whilst Pyrex glass is made not only into flasks and beakers, but is also pressed into dishes for cooking-ware.

Under heat-resisting glassware, we include articles which not only have a high softening-point but will also withstand sudden changes of temperature—combustion tubing, and tubing for high temperature thermometers, chemical ware, lamp and gas chimneys, globes and cooking-ware.

	Kavalier combustion tubing.	Jena miner's lamp.	Jena incandescent gas chimney.	Austrian "Sun Brand" chimney.
SiO_2 .	79·57	73·08	73·88	76·78
B_2O_3 .	—	17·22	16·48	—
Al_2O_3	0·04	1·98	2·24	0·72
Fe_2O_3		0·15		
CaO .	7·80	trace	trace	6·52
MgO .	0·11	trace	trace	0·24
Na_2O .	0·66	7·76	6·67	11·14
K_2O .	11·60	—	trace	4·74
As_2O_3 .	—	—	0·73	—
MnO .	—	—	trace	—

Compositions of

	Gauge glasses.			Oven ware.	
	Jena "*Durabax.*"	Jena "*Durax.*"	British.	"*Pyrex.*"	Corning Glass Works.*
SiO_2 .	67·7	72·3	71–77	80·6	56–57
B_2O_3	7·4	11·9	7·2–12·1	11·9	5
Al_2O_3	11·6	5·6	3–9	2·0	15–20
ZnO .	—	—	0–4·9	—	—
CaO .	5·6	—	0·2–0·5	0·2	5
MgO	—	—	0–1·5	0·2	12
Na_2O	7·6	9·7	1·2–5·1	3·8	1
K_2O .	0·3	0·4	0·8–5·2	0·6	—

* B.P. 477460, 477585, 477593, 479173: all of 30th June, 1936.

(4) **Optical Glass.**—(*See* p. 606.)

(5) **Coloured Glass.**—The range of colours which it is possible to impart to glass is very great. If we include white or opal, it is possible to divide the coloured glasses into groups according to the origin of the colour.

(*a*) *Coloured Silicates.*—A number of oxides produce coloured silicates, *e.g.* Green: ferrous oxide, uranium oxide (fluorescent), chromium oxide and (at high temperature) manganese oxide. Blue: cobalt oxide and copper oxide (the latter under oxidising conditions). Pink or purple: manganese oxide and nickel oxide.

(*b*) *Colour Due to Colloidal Solution or Suspension.*—The ruby colours due to gold, copper or selenium, are good examples. Each reagent is added to the batch mixture as a salt, accompanied by a reducing agent (although the selenium may be added as such or may be reduced by the furnace flame alone). When first made, the glasses are either colourless or have a light straw colour, but, on reheating, the ultra-microscopic particles of gold, copper or selenium, grow larger by segregation leading to the production of the ruby colour. If the last treatment is continued, the colour will ultimately become brown and finally, in the case of gold and copper rubies, visible particles may appear, resulting in the production of *aventurine* glass with copper-containing glasses having a high Cu content.

Amber colours, due to colloidal carbon and possibly also producible by colloidal sulphur; and yellow, due to silver, are further examples.

(*c*) *Opals Produced by Separation of an Emulsion.*—The calcium phosphate (bone-ash) opals appear to be due to this cause, the phosphate dissolving initially at high temperature and being precipitated from solution at a lower.

(*d*) *Opals Produced by Inclusion of Air or Gas Bubbles.* See B.P. 364529, 364554, 25.6.30.

(*e*) *Opals Produced by Devitrification.*—The devitrification may be due to deposition of silica, when the effect may vary from a mere cloudiness or smokiness to actual opalescence. Opal may also be formed by the separation of masses of $CaSiO_3$ or other silicates in very small crystals. The opacifying material in most commercial opal glasses is now believed to be a mixture of sodium and calcium fluorides.

The Raw Materials for Glassmaking.

The raw materials for glassmaking may be classified as—

I. Fundamental materials, or those which yield the acid and basic oxides comprising the main substance of the glass: SiO_2, B_2O_3, P_2O_5, Al_2O_3, Na_2O, K_2O, Li_2O, CaO, MgO, PbO, BaO, ZnO, FeO, and Fe_2O_3.

II. Fluxes: As_2O_3, Sb_2O_3, B_2O_3, $Na_2B_4O_7$, CaF_2, K_2SiF_6, $NaNO_3$, KNO_3, $(NH_4)_2SO_4$.

III. (*a*) Colouring agents: CuO, FeO, CoO, MnO_2, Se, C, S, $AuCl_3$, NiO, Cr_2O_3, V_2O_5, Nd_2O_3, Pr_2O_3, $Na_2U_2O_7{,}6H_2O$.

(*b*) Decolorisers: MnO_2, Se, As_2O_3, Sb_2O_3, NiO, CeO_2, CoO.

(*c*) Opacifiers: SnO_2, $Ca_3(PO_4)_2$, Na_3AlF_6, CaF_2, Na_2SiF_6, ZrO_2, As_2O_5.

IV. Oxidising agents: $NaNO_3$, KNO_3, BaO_2, Pb_3O_4, MnO_2.

V. Reducing agents: C (as coal, coke or other form of carbon), Zn, Al, Rochelle Salt, SnO.

It is to be understood that the basic oxides referred to above are generally used in the form of their salts. Only the more important materials are commented on in the section which follows.

Acid Oxides and their Sources.

Silica.—Sand constitutes the only really important source of the silica which is present, in the majority of lead glasses, to at least 55%, and in calcium and other glasses to not less than 66%. The degree of purity demanded in a sand varies with the type of glass to be made. Iron oxide is the impurity least desired by the glass manufacturer. It may be present as hydrated oxide, limonite ($Fe_2O_3{,}H_2O$) or may be associated with clay material, in bot of which cases it may be reduced by washing; or again, as a definite iron-containing mineral, such as ilmenite, in which case separation is difficult.

The use of separating tables, *e.g.* Wilfley type, is sometimes found to give a good separation of heavy mineral particles from the sand whilst some can be removed by magnetic separation. For chemical methods, *see* B.P. 325386.

For optical glass, the amount of iron oxide (as Fe_2O_3) should not exceed 0·01%; for the best tableware, not be more than 0·02%; for second grade tableware and chemical glassware up to 0·08 or even 0·1%; good quality colourless containers 0·04%; window glass 0·1–0·15%; for dark-green bottle glass as much as 2–3% or even more. For practical purposes, there are no workable deposits of sand in the United Kingdom capable of satisfactory use for good optical or the best tableware glass. Excellent sands are found in France at Fontainebleau; in Germany at Hohenbocka and Nievelstein; in the United States at Berkeley Springs, West Virginia, and at Ottawa, Illinois, with good sands also at various locations in Pennsylvania, New Jersey and Massachusetts. Belgium has excellent sand. The best British sands, at present, come from Loch Aline, Reigate, Fairlight, King's Lynn, Aylesbury and Leighton Buzzard.

The following table states the composition of samples examined:

Sand.	SiO_2.	Al_2O_3.	Fe_2O_3.	TiO_2.	CaO.	MgO.	Na_2O.	K_2O.	Loss on ignition.	Remarks.
Dörentrup	99·49–99·87	0·05–0·11	0·004–0·01	—	0·02	trace	0·003–0·09		0·12	—
Nievelstein	99·97	—	0·009	—	0·01	0·006	—	—	—	—
Hohenbocka	99·71	0·04	0·014	—	—	0·005	0·04	—	0·04	—
Fontainebleau	99·62	0·163	0·017	—	0·02	trace	—	—	0·12	—
Dutch: silver sand.	99·19	0·20	0·009	0·01	0·16	trace	0·12		0·15	—
Dutch: white sand.	99·17	0·16	0·013	0·05	0·12	trace	0·12		0·14	—
Belgian	98·64	0·62	0·03–0·04	—	0·31	0·13	0·45	trace	0·12	—
Reigate	98·93	0·67	0·04–0·05	N.D.	trace	nil	N.D.		0·28	—
Fairlight (washed).	99·47	0·24	0·034	N.D.	0·29	trace	N.D.		0·20	—
Lynn, Boam's "Chempur."	99·22	0·27	0·02	0·05	0·06	0·06	0·08		0·13	—
Lynn, Boam's double washed.	99·82	0·56	0·04–0·05	—	0·16	0·02	—	—	0·33	—
Aylesford	99·33	0·31	0·12	trace	0·04	trace	0·22	trace	0·12	—
Waen	96·63	0·41	0·03	—	0·16	—	0·26	trace	0·28	Crushed rock.
Levenseat	99·24	0·39	0·08	0·09	0·05	0·03	0·14		0·04	—
Kinghorn	92·92	1·50	1·38	trace	1·90	0·60	N.D.	N.D.	1·32	—
Muckish Mt.	99·55	0·17	0·02	N.D.	0·20	trace	—	—	0·16	Crushed rock.
Ottawa, Ill.	99·48	0·16	0·02	—	0·11	0·05	—	—	0·13	—
Berkeley Springs.	99·65	0·11	0·02	—	0·12	trace	—	—	0·23	—

For British resources, *see* P. G. H. Boswell, "Memoirs on British Resources of Sands and Crushed Rocks Used in Glass Making," Longmans Green & Co., London, 1918; *also* W. E. S. Turner, J. Soc. Glass Tech. 1940, **24**, 197.

For optical glass, and, generally speaking, for the finest tableware glass, impurities should be absent as far as possible, and the percentage of silica reach 99·5%. Except for iron oxide, the other impurities may even be an advantage in the glass when optical glass is not in preparation, whilst the iron oxide is a useful constituent when dark bottle-glass is to be made.

The size of the sand grain is also of importance. No particles should be incapable of passing a 20-mesh sieve, and a good sand is one which consists mainly (more than 90%) of particles between 30 and 70-mesh, I.M.M. or the equivalent B.S.I. sizes. The coarse particles are difficult to melt; the very fine material contains a greater proportion of impurity and may entrap fine air bubbles.

The specification of the Society of Glass Technology stipulates that sand for best colourless glass shall not contain more than 4% moisture and when dried shall contain not less than 99·4% SiO_2 and not more than 0·02% iron expressed as Fe_2O_3. TiO_2 must not exceed 0·05%, and all other colouring oxides must be absent. For sand for colourless containers and the like, the SiO_2 minimum is 98·5% and Fe_2O_3 maximum 0·04%. The gradings specified are:

Remaining on No. 18 B.S.I. Sieve—Nil (for containers No. 16 B.S.I.).
Remaining on No. 25 B.S.I. Sieve—Not more than 1%.
Remaining on No. 36 B.S.I. Sieve—Not more than 5%.
Passing No. 120 B.S.I. Sieve—Not more than 5%.

Boric Oxide is added variously as borax, boric acid H_3BO_3, and as oxide, B_2O_3, the first-named being usable only when the glass contains sufficient sodium oxide to permit part of it to be introduced as borax. The borax may be added as the decahydrate, as a "calcined borax" with about 22% H_2O, or as borax glass (anhydrous borax or "*Pyrobor*") with about 1% H_2O. A crude borax in the form of *rasorite* is used to some extent for making container ware. A typical percentage composition is: B_2O_3 45·5, Na_2O 20·0, H_2O 26·0, Al_2O_3 0·7, Fe_2O_3 0·15–0·3, CaO 1·0, MgO 1·0, "Insoluble" 5·5. The oxide is usually too expensive. Boric oxide bestows great resistance to corrosion by water, and a small amount (1%) greatly improves lead tableware glass in this respect, whilst the best glass for water gauges and chemical and heat-resisting ware also contains it as an essential constituent. The beneficial effect reaches a maximum with 12 to 15% B_2O_3 in simple soda borosilicate glasses but beyond this point durability deteriorates with addition of B_2O_3. It reduces viscosity, serves as a valuable flux and is a good solvent for colouring materials. Accordingly, some colours which are due probably to colloidal solution are not readily developed in presence of boric oxide.

Phosphoric Oxide is rarely met with in any considerable amount. It is employed in special optical glasses (*e.g.* phosphate crowns) intended for use in protected portions of optical apparatus. Most phosphate glasses are readily attacked by atmospheric moisture and weathering agencies.

It is also used sometimes in small amounts in glass for tableware as it bestows on it a bright appearance. For such a purpose it has occasionally been added as bone ash but may better be added as sodium phosphate (Na_2HPO_4). For optical glass, meta-phosphoric acid is the form employed. Phosphate glasses, in which the chief acid oxide is silica, are the opal glasses produced by the addition of bone ash or calcium phosphate.

Arsenious Oxide (As_2O_3) (technically "arsenic") and **antimony ozide** (Sb_2O_3) may be classified under the acidic oxides. Alumina probably also exercises an acidic function, but it is dealt with below under basic oxides.

BASIC OXIDES.

Calcium Compounds.—Calcium may be added as carbonate, oxide or hydrated oxide. Precipitated carbonate and powdered calcite (limespar) may be used where impurities must be excluded. Chemical lime and soap waste (both industrial by-products) as well as limestone, are used for common bottle glass, though the by-products are rarely encountered nowadays as their variable composition leading to similar variations in glass composition does not suit the stringent demands of mechanical-forming processes. Burnt lime is largely used in American glass practice; slaked lime is used occasionally in Great Britain.

Unless for dark green bottle-glass, the impurity to be avoided is iron oxide. Precipitated calcium carbonate usually has negligible quantities of iron oxide, alumina and silica; limestone may have larger amounts of each of these impurities, and the iron may to some extent be introduced during the grinding of the limestone. When used for ordinary colourless glass, the iron oxide content should not exceed 0·04%. In the limestones, organic matter and some phosphate may be present. Magnesia may or may not be considered as an impurity. In some cases it is deliberately added as dolomite limestone, in America as burnt dolomite.

Calcium carbonate in all of its various forms has the advantage of evolving gas during the glass-melting operations, thus assisting in the stirring of the molten material. Burnt lime must be used quickly owing to its adsorption of moisture and carbon dioxide; to a smaller degree slaked lime deteriorates also. On the other hand, burnt lime appears to dissolve more quickly than limestone in sodium carbonate and it is also free from organic matter.

The Society of Glass Technology's specification states (J. Soc. Glass Tech. 1937, 21, P, 111):

I. Limestone for Making Colourless Glass in Tank Furnaces.

Moisture: not more than 2% as received. *Grading*: not more than 25% passing 120 B.S.I. Standard Sieve. *Composition*: $CaCO_3$ not less than 98·5%; Fe_2O_3 not more than 0·04%; C not as carbonate not more than 0·1%; total non-volatile matter (N.V.M.) insoluble in HCl 1·0%.

II. Limestone for Making Colourless Glass in Pots.

Composition and Moisture: as I. *Grading*: all to pass $\frac{1}{8}$-in. mesh and not more than 5% remaining on 14 B.S.I. Standard Sieve.

Magnesium Compounds.—Electric light bulbs, sheet glass, tubing for gauge glasses, chemical glassware, some heat-resisting oven ware and (in U.S.A. particularly) some colourless bottle glass, contain magnesia introduced into the glassmaking mixture either as dolomite or as calcined magnesia. Certain continental glassmaking mixtures contain talc. When used to replace lime in a soda–lime–silica glass magnesia in moderate amount (up to 3% in the glass) reduces the annealing temperature and gives a longer range of temperature over which the glass can be manipulated in the forming operation.

Sodium Compounds are introduced as sodium carbonate (technically soda ash), sodium sulphate ("Saltcake"), sodium nitrate (technically "soda nitre" and "Chili nitre") and borax. All of these serve as a source of sodium oxide for the glass, and the other constituents of the salt escape as gaseous-products except in the case of borax which, in addition, serves as a source of boric oxide.

Practically all the soda ash employed is manufactured by the ammonia-soda process. It may be "dense alkali" or "light alkali" dependent on its apparent specific gravity. The former is preferable. A variety "Special for Glass Manufacture" is available which contains less very fine material than the dense ash and has become the normal source of soda for glassmaking.

The impurities are sodium chloride and small amounts of iron oxide and sodium sulphate. Soda ash is one of the most trustworthy products a glass manufacturer has to deal with.

Sodium sulphate or saltcake had a great vogue in making bottle glass in Great Britain until the early 1920's, and is still used to some extent in making flat glass. It was and still is cheaper than soda ash per unit of Na_2O, but the considerably higher temperatures needed for successful melting and the greater corrosive action on the refractory materials have led to the substitution of soda ash almost entirely as regards container manufacture and very largely as regards that of flat glass. Another point against the use of saltcake was that about 5% of its weight of coal was necessary to effect complete decomposition but the precise amount varied with furnace conditions. Too little caused saltcake to float on top of the glass, attacking the refractories, and too much produced an undesirable tint in the glass. In melting soda-lime–silica glasses, *e.g.* 5–10 parts per 1,000 of sand in the batch, are often used for preventing scum on the surface and for speeding up refining.

The saltcake used in glassmaking is not always as pure as the soda ash available, notable amounts of chloride, bisulphate, insoluble matter (iron oxide, calcium sulphate) and water being encountered. A good average sample should contain 95–96% Na_2SO_4, and not more than 0·1% Fe_2O_3. Glass made with saltcake as sole source of Na_2O takes longer to prepare than that from soda ash.

Sodium nitrate has a m.p. of 315° and therefore serves as a flux, whilst as an oxidising agent it prevents lead oxide in lead batches from being reduced to metallic lead and also hinders the development of the green ferrous silicate. It is added only in conjunction with sodium carbonate; that is, it provides only the minor proportion of the total sodium oxide content.

Borax, as $Na_2B_4O_7$, serves also as a source of boric oxide. It seldom provides more than a small proportion of the total sodium oxide.

Potassium Compounds.—Potassium carbonate is the chief source. It may be added as K_2CO_3 or (to a much smaller extent nowadays) as the hydrated form K_2CO_3,H_2O. The usual impurities are small amounts of potassium chloride and sulphate and possibly sodium salts. When used for making lead glass containing 30% or more PbO the amount of SO_3 left in the glass must not exceed 0·2% if the danger of producing opalescence is to be avoided. In the case of chloride the limit is 0·5% Cl in the glass. Potassium nitrate and sodium nitrate are used for similar reasons and in like proportions. For chemical glassware, where the presence of alumina is also desired, potassium may conveniently be added in the form of potash felspar (orthoclase) $K_2O,Al_2O_3 6SiO_2$. Such felspars always contain some Na_2O, a typical potash spar analysing SiO_2 66, Al_2O_3 18, Na_2O 3, K_2O 12% with small amounts of Fe_2O_3 and CaO.

Lead is generally introduced as red lead, Pb_3O_4, but sometimes as litharge. Lead disilicate has been used to a smaller extent. The darker variety of red lead, containing an appreciable amount, *c.* 25% PbO_2, is preferred by some glass manufacturers. Beyersdorfer's process is claimed to provide a cheaper source of lead oxide. This consists in melting pig lead in a closed pan provided with an agitator and then adding sand and continuing the heating and agitation until the sand grains are coated with a layer of oxidised lead. The larger proportion of free lead thus obtained is corrected by the use of more nitrate in the batch.

Barium Compounds.—Barium carbonate is the only one in extensive use. This may be selected natural witherite or precipitated $BaCO_3$. The latter is not always so pure as good natural material as it may contain sulphides. Barium sulphate has been used in small proportions in the U.S.A. as a refining agent for glass melting in tank furnaces.

Zinc is added in the form of carbonate or oxide.

Aluminium is added in various forms. It is generally present in smaller or larger amounts in the sand used and in the other raw materials. It is also absorbed in small amounts from the fireclay material of which the glass pots or the tank furnace blocks are made. For good colourless glass, aluminium may be added as hydrated oxide, $Al_2O_3,3H_2O$, or as calcined oxide, Al_2O_3, felspar, nepheline syenite, lepidolite, and china clay of low iron oxide content. China clay has the disadvantage of being less easy to incorporate in the batch than the other substances mentioned.

For dark coloured bottle-glass, phonolite and other minerals containing alumina, silica and alkaline oxides, ground bricks or tiles, or even dried raw clay, have been used as sources of alumina.

Opal glass is frequently made by the addition of cryolite, Na_3AlF_6.

Alumina bestows mechanical strength and resistance to chemical corrosion on glass. The addition of small amounts (1% of the total batch) may make melting easier, but beyond 5%, a hot furnace is needed for fusion, and with 10% or more the glass is not easy to work.

Colouring Agents.—These have already been enumerated. *Cobalt* is added either as the pure oxide, or, since its colouring power is great, in a diluted form, as powdered blue, zaffre (an impure basic cobalt arsenate) or smalt (a glass made from powdered quartz, potassium carbonate and cobalt oxide, containing about 2–7% of cobalt oxide. This glass is ground fine for use). Used alone, the oxide imparts a blue colour; with manganese dioxide a violet colour; and added in small quantities to copper and gold glasses, a bluish cast is given to the red colour. Cobalt oxide produces a faint blue colour when present in glass to the extent of only 1 in 100,000. One part per 1,000 produces a deep blue whilst the tint due to one part in a million is detectable in a thickness of several centimetres.

Copper for the production of blue glasses may be added as oxide CuO or nitrate. When added as sulphate (copper vitriol) a greenish-blue colour is obtained. For copper-ruby glasses, either the red oxide Cu_2O or the black oxide CuO is used in the presence of some reducing agent. In conjunction with chromium compounds, various shades of green may be obtained.

Chromium is employed most frequently in the form of oxide Cr_2O_3, and potassium chromate or dichromate. Care has to be taken, especially with the oxide, to mix thoroughly with the batch owing to its limited solubility. In lead glasses a yellowish-green, and in calcium glasses a grass-green colour is obtained. Barium chromate and copper chromate have also been used.

Uranium, producing a greenish-yellow colour in lead glasses and a fluorescent greenish-yellow in calcium glasses, is used in the form of sodium uranate $Na_2U_2O_7,6H_2O$. Very little produces the fluorescent effect but an appreciable amount (2–5%) is needed to give a marked yellow colour in thin walled ware, and frequently other colouring agents are added to reinforce the tint and save uranium salt.

Manganese.—The dioxide is the only manganese compound employed, usually in the form of the mineral pyrolusite. Under oxidising conditions, it produces a purple colour with sodium- and a violet with potassium-glasses. Used in conjunction with ferric oxide, varying shades of red, brown and purple may be obtained, dependent on the relative amounts and total amount of the two oxides, and on the presence of oxidising or reducing conditions during melting.

Nickel oxide produces a violet colour in potassium- and a red-brown in sodium- glasses.

Selenium, used either in the form of the element or as the selenite in conjunction with a reducing agent, for example arsenious oxide, gives rise to shades of red varying from pink to ruby.

Selenium needs a reducing atmosphere, and is therefore suitable for tank furnace practice.

The Glass Batch.

General Composition.—A number of attempts have been made to establish a definite relationship between the basic and acidic oxides of a stable glass. The simple, two-component glasses composed of the sodium silicates (*Water glasses, see later*) are not sufficiently stable for the manufacture of glassware. The introduction of a di- or tri-valent oxide, such as CaO, PbO, or Al_2O_3, brings about a large increase in stability. Most commercially successful glasses contain at least three components. Benrath (Sprechsaal, 1884, **17**, 266, 343) came to the conclusion from the examination of a number of good glasses on the one hand and of faulty on the other, that, with the special exception of certain optical glasses, the normal composition of satisfactory alkali–lime–lead oxide glasses should vary between the limits

$$Na_2(K_2)Si_3O_7 + Ca(Pb)Si_3O_7$$

and $5Na_2(K_2)Si_3O_7 + 7Ca(Pb)Si_3O_7$.

E. Tscheuschner ("Handbuch der Glasfabrikation," Leipzig, 1885) deduced the following formula for a good glass containing the alkalis and alkaline earths, namely

$$xA + yE + 3\left(\frac{x^2}{y} + y\right)SiO_2,$$

where xA represents the number of equivalents of the total alkalis Na_2O and K_2O, yE of the alkaline earth oxides.

Later Koerner (Sprechsaal, 1915, **48**, 332) arrived at the conclusion that in lime-containing glasses, the proportion of silica should be greater when potash is present than is required for soda. Thus, when one equivalent of lime is present (*i.e.* $y=1$), the proportion of SiO_2 needed is $4(x^2+1)$. If both soda and potash are present, x representing the total equivalent of the alkaline oxides, and x_K represents that of K_2O, the amount of SiO_2 needed is

$$\left(3 + \frac{x_K}{x}\right)(x^2+1)$$

if Na_2O is in excess of K_2O, whilst if the reverse is the case then the SiO_2 needed is

$$\left(4 - \frac{x_{Na}}{x}\right)(x^2+1).$$

Zulkowski (Chem. Ind. 1889, **22**, 280; 1900, **23**, 108, 346) and later W. L. Baillie (J. Soc. Glass Tech. 1922, **6**, T68) also attempted to correlate durability with composition, working on the idea of the "basic excess" as determining the ratios of complex and simple silicates present in the glass. More recently O. Knapp (Glashütte, 1930, **60**, 364; Glastech. Ber. 1930, **8**, 154; Keram. Rundschau, 1932, **40**, 659) has claimed that in relating properties to composition better results are obtained by assigning factors to silicates and not to oxides.

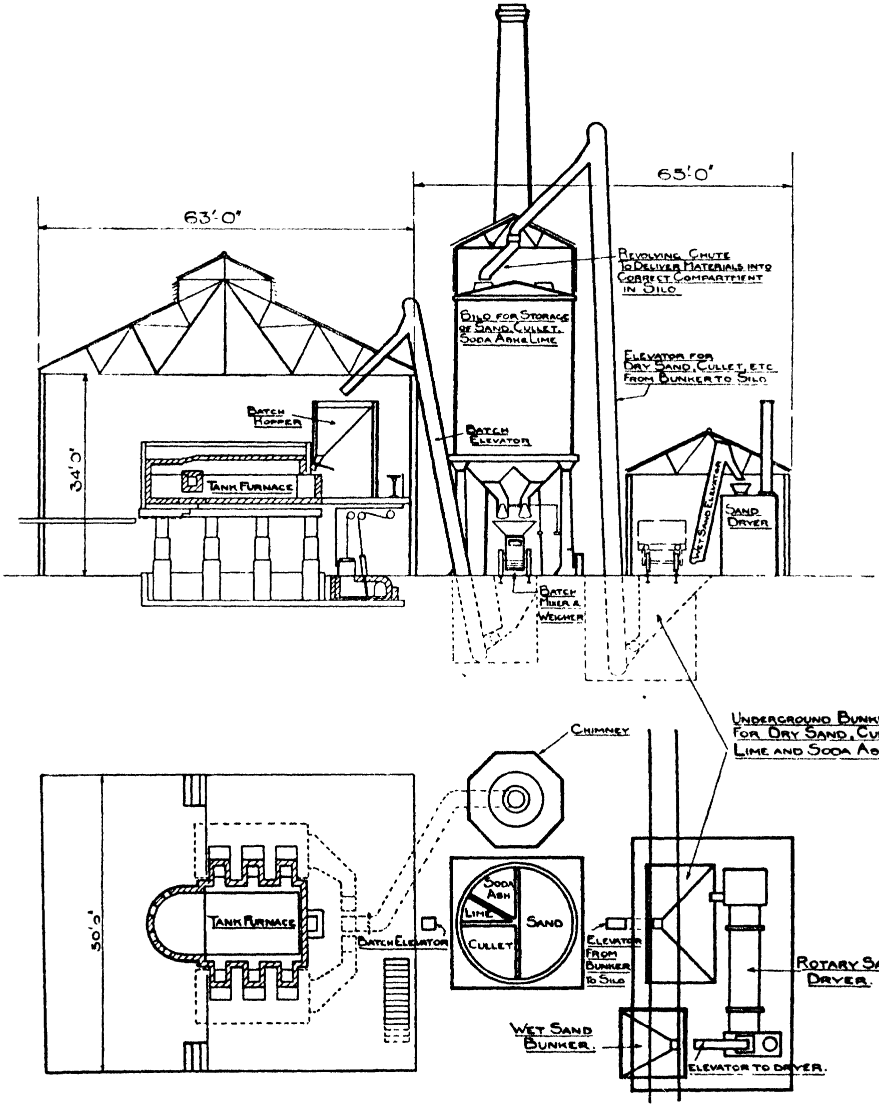
Certainly it is true that a calcium glass of the composition $6SiO_2$, CaO, Na_2O shows great stability, and many of the commercial calcium-containing glasses may be represented approximately by the so-called trisilicate formula, in which, for each $3SiO_2$, the CaO does not fall below 0·3 molecule.

Whilst experience in the past appears to have led to this adoption of a trisilicate formula, it does not follow that for modern methods of treatment, it gives the most suitable glass. Peddle (J. Soc. Glass Tech. 1920, **4**, 45) recommends a sodium–calcium glass of composition $5SiO_2$, CaO, Na_2O for many types of hollow ware. Pyrex glass, on the other hand, contains as much as 92% of acidic oxides.

Preparation of the Batch.—In modern plant specialising in the production of a limited variety of articles, such as bottles, the various raw materials are stored in large, concrete bins, arranged in a row, and at an elevation from the ground sufficient to permit of a truck or waggon to run beneath and collect from each bin the required quantity of material for the mixture or batch. In one system, a weighing machine mounted on a motor-driven truck propelled along a track below the storage bins, carries a cylindrical drum. By means of a series of indicators set by the management, several materials may be weighed separately into the drum, and when the required amounts have been obtained the drum is rotated by a second motor and the batch thoroughly mixed. The mixture is then emptied down a grating on to a conveyor belt which carries it to hoppers suspended over the feeding end of the furnace. Using such a system, one man can mix sufficient batch to maintain six large tank furnaces in continuous operation. Some factories, particularly in the U.S.A., have even more elaborate arrangements in which the batch materials flow on to a moving belt through orifices, controlled by relays operated by the belt to discharge the correct amount per unit time, so that the proper weights of each material reach the hopper discharging into the mixer. Great care is taken in many plant to eliminate dust during mixing and handling. In the U.S.A. there is at present a marked tendency to transport mixed batch to the furnace by monorail in hoppers holding a "unit batch" all of which is charged into the furnace within a short time of mixing rather than to employ conveyors, with the consequent risk of (*a*) "unmixing" the batch by vibration, and (*b*) of segregation in discharging from the much larger storage hoppers used in the conveyor method. A few factories, *e.g.* the Ford works at River Rouge add bonding agents such as water and sodium silicate to the batch and press it into briquettes in order to reduce dust and segregation, claiming also greater ease of melting. The considerably simpler process of using batches containing 1–2% moisture in the case of soda-lime-sand or 4% in alkali–lead oxide–sand batch mixtures has much to commend it from this point of view. Fig. 10 shows a layout typical of a large well-organised factory.

In other, simpler systems, the materials are weighed out into a truck and emptied into a mixing machine such as the Smith mixer, specially made for the purpose, consisting of a short cylinder with truncated conical ends, like some types of concrete mixer.

At least two other types of mixing machine are also used in batch preparation. The first is a trough mixer of the Gardner type in which mixing or kneading blades revolve on a shaft running through a horizontal trough, and the second, which in recent years has assumed considerable importance, is the so-called counter-current mixer of which the Eirich machine was an early example. In this type a pan is revolved about a vertical axis and a spider carrying mixing ploughs and crushing rolls is driven in the opposite direction. The various ploughs divert the material either to or from the centre of the pan and the roll or rolls are set to crush any aggregates that may be present, but not to reduce the fineness of the material.


63'-0"
65'-0"
34'-0"
50'-0"
Batch Hopper
Tank Furnace
Batch Elevator
Revolving Chute To Deliver Materials into Correct Compartment in Silo
Silo for Storage of Sand, Cullet, Soda Ash & Lime
Elevator for Dry Sand, Cullet, etc From Bunker to Silo
Sand Dryer
Wet Sand Elevator
Batch Mixer & Weigher
Underground Bunkers For Dry Sand, Cullet, Lime and Soda Ash
Chimney
Tank Furnace
Batch Elevator
Soda Ash
Lime
Sand
Cullet
Elevator From Bunker To Silo
Rotary Sand Dryer.
Wet Sand Bunker.
Elevator to Dryer.

(*Stein and Atkinson.*)

FIG. 10.

Where the number of types of glassware made in a factory is so large that many different batches have to be made up, as in certain pot-furnace works, a correspondingly small mixing plant is used, and may consist merely of a rectangular box rotating on an axis passing through one diagonal, or even of a simple barrel. Hand mixing is often employed, particularly when extreme purity of materials must be preserved, as in mixing optical-glass batches. In this case the materials are weighed out into a wooden trough and mixed by a wooden scoop or shovel.

Batches for Different Types of Glass.—The following batches will serve to indicate the general proportions of the various constituents used in making different glasses, especially illustrating the amounts of colouring, opacifying or decolorising materials required. Whilst they have actually been employed in practice, it does not follow that the batches represent the best possible for any particular type of operation.

The terms soda ash and potash, used below, correspond to anhydrous sodium carbonate (58% alkali) and potassium carbonate respectively.

I. LIME-CONTAINING GLASSES.

A. Bottles.

(1) *Quick-Setting Glass for Large Hand-Made Beverage Bottles.*—Sand 1,000, limestone 500, soda ash 300, saltcake 100.

(2) *For Owen's Machine.*—Sand 1,000, soda ash 360–375, limestone 175–240, dolomite 0–20.

(3) *O'Neill, Lynch and other Feeder-fed Machines.*

(*a*) *Colourless.*—First-grade sand 1,000, felspar 0–100, soda ash 375, limespar 180–220, borax 0–30, saltcake 0–7, arsenious oxide 1, powdered blue 0·06, selenium 0·03.

(*b*) *Amber-Coloured Glass.*—Sand 1,000, soda ash 360–380, limestone 180–220, saltcake 8, carbon (as coal or coke) 10, graphite 1.

B. Cheap Glass for Common Pressed Tumblers.

(1) Sand 1,000, soda ash 400, limespar 180, arsenious oxide 1, selenium 0·03. Cobalt oxide or powder blue, *q.s.*

(2) *Medium Quality Glass Tumblers.*—Sand 1,000, soda ash 300, potash 50, limespar 100, baryta 100, potassium nitrate 50, manganese dioxide, *q.s.*

(3) *Common Light Wall Tumblers.*—*See* Batch, under C. below.

C. Electric Light Bulbs.

Sand 1,000, felspar 270, dolomite and limestone 230, soda ash 380, potassium nitrate 35, manganese dioxide 0·5, nickel oxide 0·02.

D. Window Glass.

(1) Sand 1,000, soda ash 260, saltcake 60, limestone 370, coal 2–3.

(2) Sand 1,000, soda ash 350, limestone 90, dolomite 205, felspar 95. (Part of soda ash may be replaced by saltcake.)

(3) (Briquetted batch for Ford Process.) Sand 1,000, limestone 292, soda ash 315, saltcake 73, charcoal 5·6, waterglass (42° Bé) 40, water 40, cullet 225.

II. LEAD-CONTAINING GLASSES.

A. Best Crystal Glass for Tableware (English Crystal).

(1) Fontainebleau (or equal grade) sand 1,000, potash 330, borax 30, potassium nitrate 40, red lead 660, arsenious oxide 2·5, manganese dioxide 0·2–0·3.

(2) *Semi-Crystal.*—Fontainebleau (or equal grade) sand 1,000, potash 350, limespar 140, red lead 100, nickel oxide 0·02.

B. Electric Light Bulbs.

Fontainebleau sand 1,000, soda ash 330, red lead 480, borax 90, felspar 70, sodium nitrate 50, manganese dioxide 2.

III. CHEMICAL, GENERAL SCIENTIFIC AND ILLUMINATING GLASSWARE, GAUGE GLASSES.

A. Glass Tubing for General Chemical Purposes.—Sand (<0·04% Fe_2O_3) 1,000, felspar 367, limespar 220, soda ash 448, potash 151, magnesia 4, manganese dioxide 2·75.

B. Beakers, Flasks, etc.—Sand (<0·04% Fe_2O_3), 1,000, hydrated alumina 182, limespar 182, mangnesia 15, potassium nitrate 30, soda ash 150, calcined borax 185.

C. Gauge Glass Tubing.—Sand 1,000, felspar 350, magnesia 40, borax (granulated) 500, potash nitre 20, arsenious oxide 10.

D. Ampoule Tubing.—Sand 1,000, alumina 230, limestone 170, dolomite 30, borax (granulated) 300, soda ash 125, potash nitre 30.

IV. OPTICAL GLASS (*see* p. 606).

V. COLOURED GLASS.

A. White, Alabaster or Opal.

(1) *Alabaster.*—Sand 1,000, red lead 560, soda ash 490, sodium nitrate 50, sodium chloride 50, sodium fluoride 75, calcined alumina 225, felspar 1,200, antimony oxide 5.

(2) *Cryolite Opal.*—Sand 1,000, soda ash 230, potash 40, cryolite 100, felspar 100, fluorspar 100, arsenious oxide 5.

(3) *Bone-Ash Opal.*—Sand 1,000, potash 300, soda ash 70, bone ash 300, limespar 100.

(4) *Milk White Glass for Lamp Shades.*—Sand 1,000, soda ash 150, felspar 180, fluorspar 90, cryolite 80, tin oxide (SnO_2) 40.

B. Black Glass.

Sand 1,000, potash 100, soda ash 250, limespar 150, manganese dioxide 100, copper oxide 80, cobalt oxide 40, hammer scale (Fe_3O_4) 40.

C. Red Glass.

(1) *Gold Ruby.*—Sand 1,000, red lead 440, potash 290, borax 200, gold chloride 0·36. Sometimes bone ash, pyrolusite and iron oxide are added in small amounts.

(2) *Copper Ruby.*—Sand 1,000, potash 200, red lead 300, cupric oxide 3, stannous oxide 10.

(3) *Selenium Ruby.*—Sand 1,000, potash 300. soda ash 300, zinc oxide 200, cadmium sulphide 15, selenium powder 10–15, borax 15 (less alkali than this is used in many cases). In these cases the ruby colour is generally developed on reheating the glass at the mouth of the furnace or during passage down the annealing lehr.

D. Yellow Glass.

(1) *Amber Yellow.*—Sand 1,000, soda ash 250, potash 100, limespar 160, sulphur 15, arsenious oxide 5.

(2) *Orange Yellow.*—Sand 1,000, potash 120, soda ash 190, limespar 145, potassium nitrate 5, uranium oxide 3, selenium 0·6, arsenious oxide 2·5.

(3) *Canary Yellow* (*Opal*).—Sand 1,000, potash 300, red lead 150, limespar 90, potassium nitrate 50, calcium phosphate 30, borax 15, sodium sulphide 7·5, Rochelle salt 7·5, cadmium sulphide 30.

E. Green.

(1) *Vegetable Green.*—Sand 1,000, soda ash 360, limespar 180, potassium chromate 6·5, hammer scale 4, arsenious oxide 4.

(2) *Golden Green.*—Sand 1,000, potash 100, soda ash 200, burnt lime 140, red lead 30, cupric oxide 5, uranium oxide 12·5, arsenious oxide 5.

(3) *Aventurine Green.*—Sand 1,000, soda ash 350, felspar 220, fluorspar 100, barium carbonate 180, potassium dichromate 120, manganese dioxide 60.

F. Blue.

(1) *Dark Blue.*—Sand 1,000, soda ash 350, limespar 160, cobalt oxide 2.

(2) *Aquamarine Blue.*—Sand 1,000, potash 50, soda ash 250, limespar 16, copper vitriol 20.

(3) *Azure Blue.*—Sand 1,000, potash 200, limespar 120, cryolite 120, copper vitriol 45, smalt 5.

Sand of high grade is desirable in most cases for producing coloured glasses.

Any batch taken from a list such as the above may require adjustment to suit the article for which it is to be worked and the normal temperature of the furnace. The colour also depends on: (1) the freedom of the sand or other raw materials from iron oxide; (2) the presence of oxidising or reducing conditions; (3) the nature of the other constituents present. Thus, as previously indicated, the same colouring agent frequently yields somewhat different colours according as the glass contains lead or calcium, or according as the alkaline element is sodium or potassium.

In general, closed pots are most suitable for coloured glasses, although cobalt blue, iron oxide green, vegetable green and certain shades of amber can be made successfully in tank furnaces.

In addition to the raw materials stated above, it is usual to add a proportion of previously melted glass or cullet. The amount may vary between 20 and 50% of the weight of the raw batch. Whatever amount is used it should be kept constant and should be added in reasonably small fragments, particularly if it is not of precisely the same composition as the glass to be melted. It is good practice to pass cullet through a jaw crusher and, if for colourless glass, to remove iron by electromagnetic separation before mixing with the batch.

The Melting of Glass.

A. REFRACTORY MATERIALS USED IN MAKING POTS AND TANK-FURNACE BLOCKS.

The most important raw material is fireclay and the compositions of various types are given in Table VIII. It should be noted that the clay in any of the localities mentioned may vary in composition from point to point both along and vertically across the deposit.

The clays are hand-picked to remove im-

TABLE VIII.—PERCENTAGE COMPOSITION (BY ANALYSIS) OF SOME FIRECLAYS USED IN THE MANUFACTURE OF TANK BLOCKS.[1]

	SiO_2.	Al_2O_3.	CaO.	MgO.	Fe_2O_3.	Na_2O.	K_2O.	TiO_2.	Ignition loss.
Stourbridge	55·7	27·9	0·51	0·40	1·76	0·36	0·71	1·06	11·5
Halifax	54·1	27·8	0·31	0·48	2·86	0·41	0·92	1·26	11·9
,, ...	68·8	18·9	0·19	0·41	2·31	0·32	0·74	1·14	7·1
Scotch	50·1	29·8	0·33	0·65	2·88	0·13	0·86	1·34	14·0
,, ...	50·9	40·6	0·45	0·21	3·84	0·37	0·6	—	[2]
Cornwall (China clay) . .	48·3	37·0	0·41	0·33	0·71	0·31	0·84	0·14	11·9
Dorsetshire (ball clay) . .	51·0	31·2	0·54	0·62	1·48	1·62	0·58	1·16	11·8
Belgium (Namur) . . .	49·2	32·3	1·02	0·41	2·74	1·82		1·84	10·74
,, (Delforges) . .	53·5	28·7	0·51	0·19	1·49	1·16		0·76	13·62
,, ,, . .	62·5	22·1	0·61	0·14	0·96	1·04		0·81	11·7
France (Provins) . . .	65	33	0·2–0·4	—	1·5–1·7	—		—	—
Grossalmerode	70·4	19·9	0·24	0·24	1·81	0·75		0·91	7·3
,, ...	47·5	34·4	0·5	1·0	1·2	—		—	14·4
Meissen	51·7	33·3	0·1	0·9	1·5	0·6		—	11·8
,, ...	72·3	19·3	—	—	1·0	0·3		—	7·3
Wildstein	47·9	36·3	0·2	0·1	2·2	1·5		—	11·9
Vallendar	65·3	24·2	—	—	1·0	1·2		—	6·8
Klingenberg	49·8	33·6	0·5	—	1·58	0·7		2·0	11·5
America	59·6	25·7	0·42	0·68	1·31	1·02		1·14	10·1
Andsia (St. Louis) . . .	48·5	35·0	—	0·37	—	0·68		—	9·1
Russia (Driefer). . . .	56·3	31·0	0·85	0·59	1·19	—		—	8·5
,, (Bobrik) . . .	43·1	36·4	0·39	0·10	1·14	0·61	0·20	—	17·9
Indian Sillimanite . . .	32·3	62·1	0·68	0·12	1·76	0·28		1·91	0·9

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[1] J. H. Partridge, "Refractory Blocks for Glass Tank Furnaces," 1935.

[2] Ignited sample.

purities, weathered by exposure, dried, crushed, and ground usually to pass 1·5–2 mm. aperture. Besides the raw clay, which may be plastic or "lean" depending upon its physical and chemical nature, previously fired clay called "grog" is used to reduce the drying shrinkage and to give stability during drying. To produce a dense structure by the mixture of these a variety of grain sizes of grog is needed. J. H. Partridge (Refractory Blocks for Tank Furnaces, Society of Glass Technology, Sheffield, p. 19, 1935) quotes Table IX. to show the distribution of grog size to give a mixture with densest packing, assuming spherical particles. Using such graded grog the shrinkage varies with the amount of bond clay mixed with it, but the porosity of the fired mixture decreases up to 15–20% bond clay and then increases again. The grog used may be porous itself if prepared by calcining fireclay or may be non-porous if of sillimanite, bauxite or quartzite. The mixture when wetted is well mixed in a pan mill or in a pug mill (formerly trodden by foot) and is sometimes subjected to vacuum to remove entrapped air that might spoil the dense structure desired. The relative proportions of raw clay to grog and the size of the latter depend on the purpose for which the mixture is intended. Low grog (20–35%) and fine grain is used for pot-making and similar processes whilst tank-furnace blocks are made with very high percentages of coarser grog. The raw clay is usually a mixture of a refractory clay (base clay) and one (bind clay) chosen for its binding properties. For potmaking the following has been used: Stourbridge base clay 5, Stourbridge bind clay 4, grog 2, crushed old pots 1½. The amount of water varies with the raw clay content varying from about 6–22%. When mixed the clay mass is stored to "sour" for periods up to 6 months in order to acquire uniformity and plasticity.

TABLE IX.

Relative size	x	$0·415x$	$0·225x$	$0·175x$	$0·115x$	very small
Per cent. each size needed.	77	5·5	1·7	3·3	1·0	11·4
B.S.I. sieve size	5 × 17	12 × 25	20 × 28	30 × 31	40 × 34	—
Particle size (mm.) . . .	3·6	1·5	0·8	0·63	0·41	—

Pots are built up by hand from rolls of plastic clay, raising the walls a few inches on alternate days. Alternatively they may be beaten up in plaster moulds. They may be open or "closed" and contain up to 30 cwt. of molten glass. Fig. 11 shows different types: (*a*) a closed or covered pot is used generally for the highest grades of glass melted in Great Britain. In one type, the "oval" or "dog-house" pot, the distance from the mouth to the back is considerably greater than between the side walls; (*b*) an open pot, used for plate glass and in many countries also for high quality glass, even optical glass; (*c*) a skittle pot, used in the furnace in an inclined position so that the workman can readily gather the glass; (*d*) a potette, used occasionally in tank furnaces where the charging has to be done at the sides and not at the end of the tank, and also where the temperature at the working end makes the glass too fluid. The glass from the tank flows into the potette through an opening near the bottom.

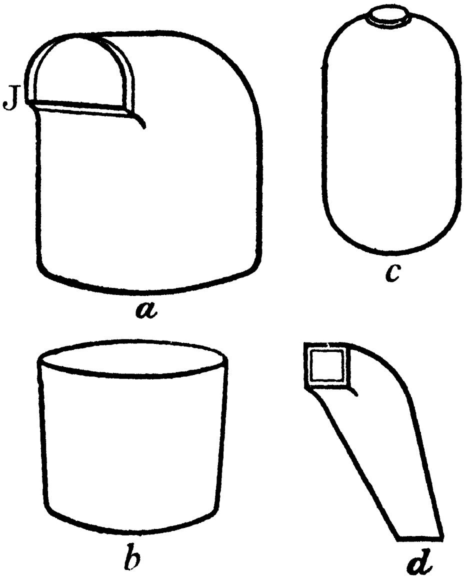


FIG. 11.

Tank Blocks are made by several processes as shown in Table X.

TABLE X.—METHODS USED FOR MANUFACTURE OF TANK BLOCKS.

Process.	Grog, %.	Raw clay, %.	Water, %.	Drying time.	Shrinkage in making, %.	True volume porosity, %.
Hand moulding, plastic .	50–75	50–25	17–22	3–4 months	4–6	27–30
Hand moulding, ramming	70–85	30–15	7–10	8–14 days	3–4	27
Mechanical ramming. .	80–95	20–5	5–8	4–5 „	0·2–2	19–20
Semi-dry pressing . .	70–85	30–15	7–10	3 „	2–5	13–26
Extrusion	As hand moulding, plastic					
Slip casting	60 (min.)	40 (max.)	16–20	2–3 months	3–4	24–35
Fusion casting . . .	nil.	100	nil	14 days (annealing)	10	4

In considering porosity, it should be remembered that the kind of pores as well as the total volume of pore space is an important factor. Mullite tank-blocks cast from electrically fused raw material to give the approximate composition $3Al_2O_3 \cdot 2SiO_2$ have been extensively used in recent years on account of their good outer texture and low rate of solution in colourless soda–lime–silica glass. Slip cast sillimanite also is much favoured. Sillimanite itself has very good corrosion-resisting properties and the main difficulty in converting it into corrosion-resistant articles is in finding a bond for the grains which will itself withstand attack. To make a slip the well-mixed dry materials are added to water in a vessel (blunger) fitted with a stirrer and when the mass begins to stiffen a small amount of electrolyte in the form of sodium silicate and carbonate is added to deflocculate the clay. This gives a mass of pouring consistency with a much lower water-content than could otherwise be obtained. The mass is then poured into moulds of wood or plaster which are stripped away after the mass has set. The best amount and proportions of electrolyte must be separately determined for each type of clay mixture used.

B. FURNACES.

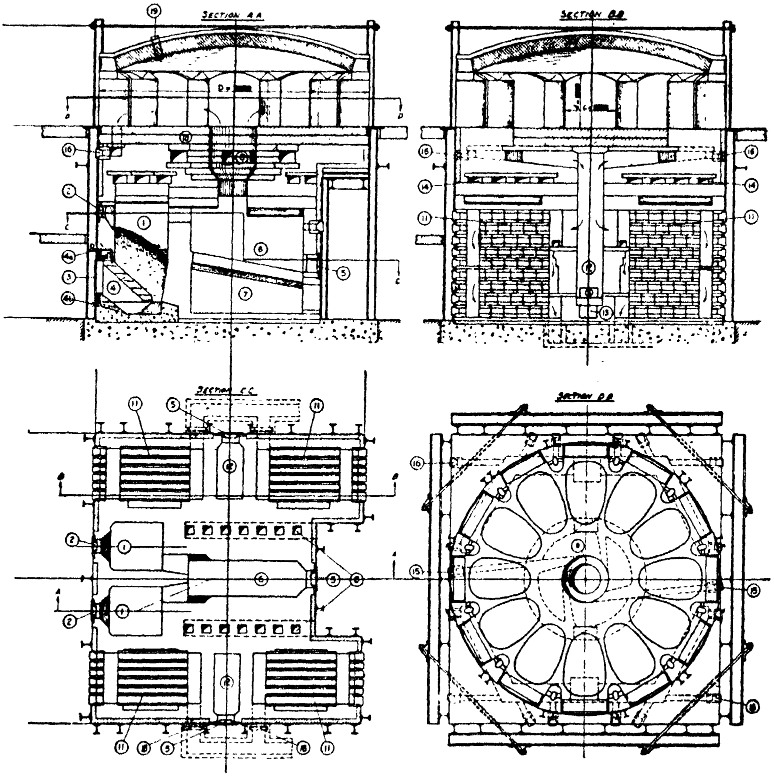
(*a*) **Pot Furnaces** are used for the preparation of the finer quality glasses and in cases where a variety of compositions are handled at one and the same time. Using closed pots, the glass melting may be conducted out of contact with furnace gases and by claying up the joint between the pot mouth and the stopper, volatile materials like selenium may be retained to a greater extent than in tank furnaces. From 1 to 20 or more pots holding 4–30 cwt. may be set in the furnace, which may be direct fired (practically obsolete), be heated by gas from an inbuilt producer, or by producer gas from a distant generator. In a few cases coke-oven gas is used for heating. The floor or " siege " consists of thick fireclay or sillimanite blocks, and its shape may be circular, oval or rectangular. Rising from the floor are arches, the pillars of which are of fireclay, sillimanite or silica bricks (generally sillimanite), and the arch is of such dimensions as to accommodate a pot of definite size. A domed roof of silica bricks called the " crown " completes the enclosure. The understructure depends on the mode of firing adopted. In the old direct-fired and the semi-gas-fired system, a circular firebox is built below the furnace opening into a circular hole in the siege called the " eye " through which flame passes from a coal fire, or round which combustion of gas should begin to reach an advanced stage. Either recuperation or regeneration is applied according to type of furnace. Fig. 12 shows a Teisen 12 pot " Tetra " recuperator furnace. The tangential burner gives good mixing of gas from the built-in producer and secondary air preheated by passage up the recuperator channels, and produces a flame filling the furnace. For a 12 pot furnace the " eye " has a diameter of 4 ft., and for an 8 pot furnace about 2 ft. 6 in. The pots are set in the arches as shown in the plan view, and the flame issuing from the eye sweeps over them, the spent gases being withdrawn through holes 17 in the pillars supporting the crown. The spent gases then travel through the recuperator as indicated by the arrows, and pass out into the chimney flue controlled by dampers 18. Great pains are taken to prevent, by the design and construction of the tube sections of which the recuperators are built up, all communication between the air passages and those for waste furnace gases. Regenerative pot furnaces are favoured where the melting schedule is such that the furnace can be driven as a whole, *e.g.* when melting in all pots overnight and working out the glass through the day. The flame may be introduced through holes in the siege, firing from end to end, or through ports in the end or side walls (horseshoe or cross-flame firing).

The pot, after being built up as already described, is allowed to dry slowly, devices being employed in modern plant to control the degree of humidity. Subsequently, the pot is stored for months in a room at about 65°F., the humidity being preferably controlled prior to use and is kept free from vibration. In preparation for the glass furnace it is first heated in a special furnace called a pot arch, in which the temperature can be raised slowly to about 1,100°C. or 1,200°C., and the moisture, combined water and carbonaceous matter, driven off. In America, the following rate of heating is considered good practice: in 1 day, 75°C.; 2 days, 120°C.; 3 days, 371°C; 4 days, 596°C.; 5 days, 816°C.; 6 days ,1,025°C.; and 7 days, 1,160°C. At the last-mentioned temperature the pot should be maintained for 30 hours.

The process of " pot setting " next follows. The pot is removed from the pot arch on a heavy iron carriage and placed carefully in position in one of the arches of the furnace, and the front of the arch closed as rapidly as possible, preferably by fireclay blocks made to fit the arch. The jib of the pot, J in Fig. 11 (*a*), is not rigidly built into the wall so erected until the pot has been well fired in the furnace. Otherwise shrinkage might throw such a strain on the jib as to cause a crack to develop just below it in the pot wall. The only part exposed is the neck or mouth of the closed pot, and into this neck or mouth a flat slab or stopper is placed. An open pot stands entirely behind the furnace wall, being worked through an opening in the latter. When in position the pot should be allowed to remain empty for at least a day at as high a temperature as possible, short of incipient softening, before being glazed and filled.

(*b*) **Tank Furnaces** are used for economical melting of large quantities of glass needed for mass-produced articles such as bottles and other containers, drawn sheet, plate, wired and other forms of flat glass, electric lamp bulbs and cheap domestic glass made by pressing. In size they may vary from a dead weight capacity of about 2 tons to 1,250 tons, the latter being the approximate capacity of one window glass tank in America. Furnaces of from 100 to 350 tons deadweight capacity are quite usual.

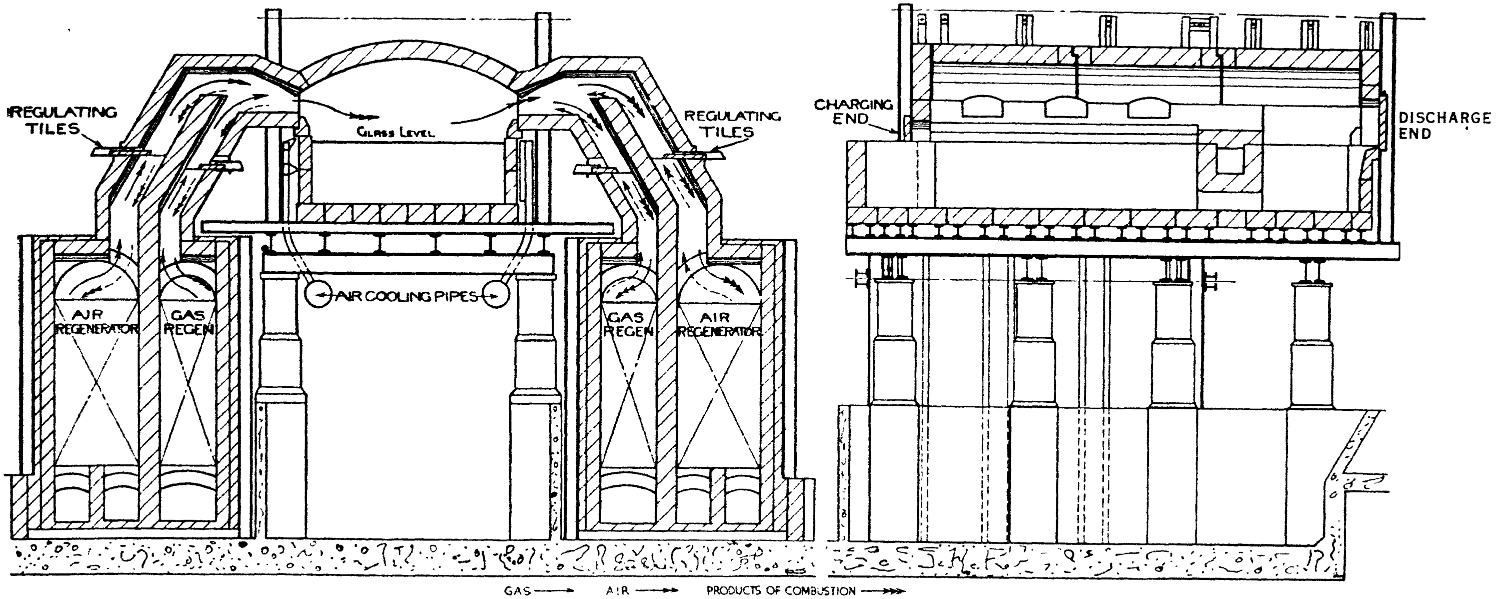
Fig. 13A represents the cross-section of a regenerative glass tank furnace. It will be seen to be similar, generally, to an open hearth steel furnace. The bottom consists of fireclay blocks resting on mild steel laths themselves laid on mild steel joists of I-section supported on piers so that air has free access to cool the bottom. The sides, usually 45 in. high, may consist of three courses of fireclay, sillimanite or fused high alumina refractory (*e.g.* Corhart), 9 in. or more in thickness, but in order to reduce wear on the refractories which is nearly always worst at horizontal joints, the top two courses may be made one by using blocks twce as deep, or a single course three times asi deep may be substituted. The crown of the furnace is of silica brick usually 12 in. thick and sometimes insulated. It may be composed of a number of suspended blocks (Fig. 13B) so that the shape and volume of the conbustion space above the glass can be controlled. The gas and air for combustion are preheated by passing through one set of regenerator chambers, say the left-hand pair, being controlled by the regulating tiles in the various uptakes on that side (up to 7 but usually 3–4 such), and mix in the port before issuing through the mouth of the latter to burn in the furnace above the glass, whilst the waste gases pass out through the opposite port, heating up the right hand regenerators on their way to the chimney. The extent of this premixing is controlled by (*a*) the relative velocities of the gas and air streams, (*b*) the angle at which they meet, (*c*) the distance from the port mouth to the point at which the two streams first begin to mingle. This distance is controlled where necessary by



(*By permission.*)

FIG. 12.—TEISEN RECUPERATIVE POT-FURNACE.

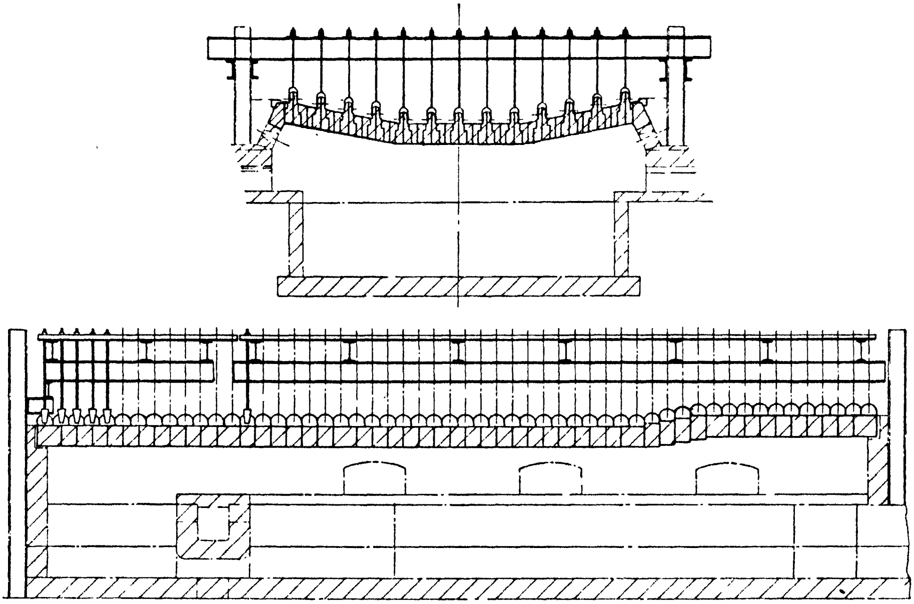
1. Built-in step grate producer.
2. Gas tight C.I. fire door.
3. Gas tight C.I. ash door with primary air regulation slide.
4. C.I. step grate standard with M.S. fireplates.
4*a*. Water inlet tubes to firebar plates.
4*b*. Water outlet pipe from ash pan.
5. Gas tight C.I. doors for glass pocket.
6. Central glass pocket.
7. Air space beneath same, preventing downward flow of glass.
8. Secondary air pocket with trap channels to prevent flow of glass into recuperator.
9. Tangential burner of specially shaped bricks.
10. Highly refractory siege blocks.
11. Four recuperators of special hexagonal tubes with horizontal waste gas and vertical zigzagging air passages.
12. Side glass pocket.
13. Air space beneath 12 preventing entry of glass into chimney flues.
14. Cooling flues above recuperator arches.
15. Inspection channels for main inlets of tangential burner.
16. Inspection stoppers in waste gas channels beneath siege.
17. Waste gas draw off holes in pillars.
18. Chimney damper.
19. Position of pyrometer tube.



(*Stein and Atkinson.*)

FIG. 13A.—SECTION VIEWS OF REGENERATIVE GLASS TANK FURNACE.

prolonging the wall shown in a substantially horizontally direction to form a *tongue* of suitable length. After running 15–30 minutes so that the right hand side regenerators become heated up, the direction of the flame is reversed, air and gas going through the right hand chambers whilst waste gas goes out through the left hand. In many modern plant this reversal is controlled not by time but by the temperature reached in the regenerators. The refractories of the port mouth above glass level are usually silica, as are the side walls above glass level. These nowadays are carried by the steelwork of the furnace so that no load rests upon the blocks actually forming the bath to contain molten glass, enabling the latter to be rebuilt as necessary without disturbing the upper structure. In normal usage a tank for melting bottle glass would have a life of at least 8–10 months and could be rebuilt many times before the upper structure needed serious attention. The space between upper and lower sidewalls is filled in by "tuckstones." The tank itself is nearly always divided into 2 parts by a bridge wall with a hole (doghole) in the middle well below glass level to permit passage of glass but not of surface impurities. Instead of this hole in the bridge some furnaces have a hole in the floor on each side of the latter joined by a "submerged throat." With some types of glass such a device is hard to keep open. In furnaces for melting sheet glass the fixed bridge is generally replaced by floating blocks which lock into each other to form a floating bridge. Several such may be used on one tank. The larger portion of the tank called the melting end has in good practice an area of about 10 sq. ft. per ton of glass melted per 24 hours, the ratio of width to length being frequently 3:5 for medium to large furnaces. The smaller portion or working end is the reservoir from which the machines draw glass properly homogenised and cooled to the working temperature. It has at least one day's capacity. The depth of both portions is generally the same, namely 3 ft. 3. in to 3 ft. 6 in. for colourless glass, though some working ends are made shallower towards the point of discharge of the glass. Batch is charged into the furnace at a "doghouse," a kind of well built out from the end (sometimes in small furnaces the side) wall. It is either tipped from barrows, poured from overhead bins *via* a chute with sliding gate, or fed by a mechanical device. In the two former cases piles are pushed by hand with long rakes below a low jack arch into the furnace, the opening being left sealed by a pile of batch. Mechanical devices either push small charges forward by a reciprocating "pusher" ("Hazel-Atlas" type) or continuously feed batch forward by an Archimedean screw ("Amco" type), or combine both motions to push forward a large pile that has been fed into an enclosed extension of the doghouse by a screw device ("Charlton" type).



(*Stein and Atkinson.*)

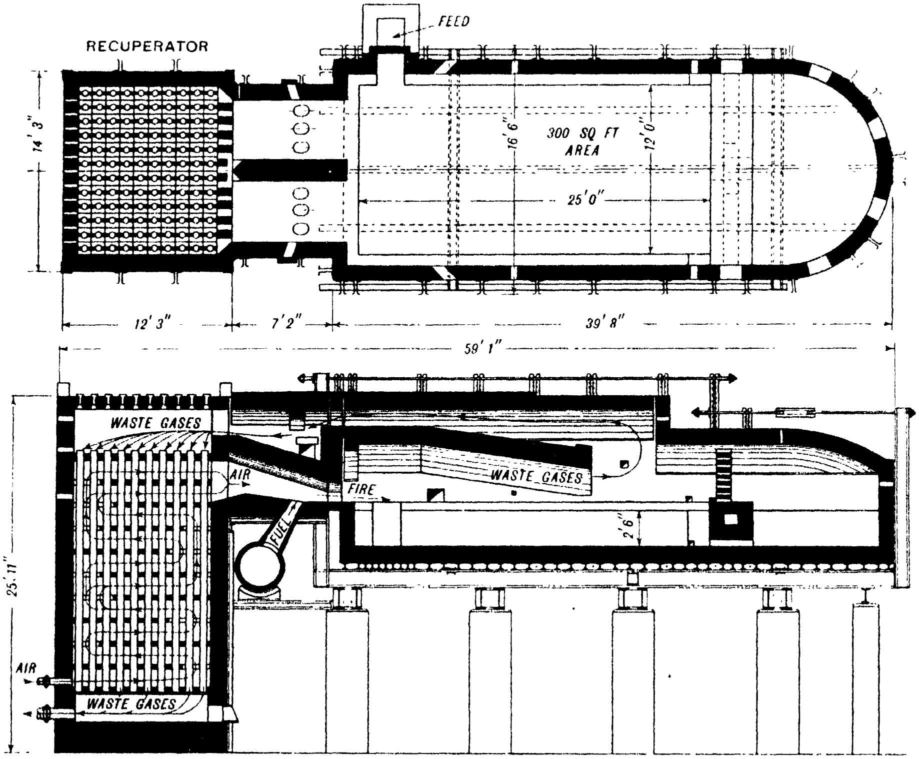
FIG. 13B.—FURNACE WITH SUSPENDED CROWN.

The recuperation principle is also applied to tank furnaces, generally to small or medium sizes. Fig. 14 shows one type in general use.

(*c*) **Electric Melting Furnaces.** V. M. Sauvageon (B.P. 18118/1909) attempted to melt glass by passing an electric current between carbon electrodes immersed in the mass. The use of metal electrodes or metal casing for the carbon was suggested. Later he devoted much work to the development of furnaces heated by radiation from refractory parts (*e.g.* the crown of the furnace) which were packed with carbon granules to form resistors. Later and more practical applications of electricity have been in two directions:

(1) *Furnaces Heated by Immersed Electrodes.*—*See* E. Meigh (J. Soc. Glass Tech. 1931, **15**, T333), J. Ferguson (U.S.P. 1979609, 1979610 of 1934, 2000278, 2006947, 2008495, 2018883, 2018884, 2018885, 2018886, 2022112 all of 1935, 2101675 of 1937), J. K. B. Raeder (B.P. 350930 of 1930), E. Cornelius (B.P. 303798, 381500 of 1932), H. F. Hitner (U.S.P. 1610376, 1610377, 1761342, 1815977, 1815978), British Thomson-Houston Co., Ltd. (B.P. 506366 of 1937), G. Slayter (U.S.P. 2212528 of 1940). Raeder used submerged carbon electrodes whilst Cornelius used submerged electrodes of very pure iron particularly low in carbon.

A Cornelius furnace of 12½ tons dead weight capacity has melted approximately 5 tons per day in a British Factory (Meigh, *l.c.*) for a period of 3 months for an average consumption of 1 kw.h. per 1·179 kg. glass. It was concluded that if electricity were available at a cost of 0·2*d*. per unit, electric melting could be made to compare favourably with that by coal. In America the Ferguson furnace has melted a resistant type of borosilicate glass very successfully with the limitation that, for economical working, the batch materials must be such that no volatile products are given off during melting. The small unit is claimed to produce between 2 and 3 lb. of glass per kw.h. depending on the composition (Turner, J. Soc. Glass Tech. 1940, **24**, T40).



(*Amco* K.T.G.)

FIG. 14.—RECUPERATIVE GAS-FIRED TANK FURNACE.

(2) *Furnaces Heated by Radiation from Resistors.*—*See* Soc. Anon. de St. Gobain (B.P. 506696, 507280 of 1938). Pot furnaces heated by numbers of vertical exposed "*Silit*" or "*Globar*" rods have been described by H. Nathusius (Brown, Boveri & Cie, Glastech. Ber. 1934, **12**, 387) and Siemens-Schuckertwerke (*ibid.* 1934, **12**, 388) in which temperatures of 1300–1400° can be obtained. The current consumption is claimed to be 2·25 kw. per kg. glass for pots of 400 kg. capacity (Brown, Boveri) and 6 kw. per kg. glass for pots of 35 kg. (Siemens-Schuckert).

C. THE MELTING PROCESS.

Reaction between the constituents of a glass batch proceeds even with the solid materials, but it is enormously facilitated by the intimate contact brought about when melting occurs. Immiscibility of constituents is rarely encountered in practice, some phosphate glasses and simple soda-borosilicate glasses are examples, but frequently immiscible layers first formed disappear with time or rise of temperature. Molten salts in general are readily soluble in one another (O. Sackur, Z. physikal. Chem. 1912, **78** 550, 564; P. Niggli, Z. anorg. Chem. 1916, **98**, 241; M. Amadori, Atti R. Accad. Lincei, 1912, **21**, II, 67; 1913, **22**, II, 332) hence the fluxing effect of such low melting-point salts as the alkali nitrates. In such a viscous medium as glass, reactions do not proceed to completion even at the melting temperature in the time usually given. For this reason equilibrium diagrams do not completely indicate what occurs when a glass batch is heated.

Volatilisation.—All water is not given off in melting, small amounts being retained most tenaciously in the glass (exclusive of surface adsorption) (E. W. Washburn, F. F. Footitt and E. N. Bunting, Univ. Illinois Expt. Sta. Bull. 1921, No. 118; H. Salmang and A. Becker, Glastech. Ber. 1927, **5**, 520; 1929, **7**, 241; R. H. Dalton, J. Amer. Ceram. Soc. 1933, **16**, 425). Chlorides of **Na**, **K**, **Fe**, **Sn**, oxides of **As**, **Sb**, **Pb**, **B**, sodium sulphate and selenium are volatile but by no means completely removed. The amount of As_2O_3 volatilised when 0·2–2% is added to a potash-lead oxide–silica glass is on the average 10–20% of that added (W. E. S. Turner and co-workers, J. Soc. Glass Tech. 1927, **11**, 66). C. E. Gould and W. M. Hampton (Glass Ind. 1930, **11**, 249) give, for their own working conditions, the following figures for the volatilisation loss per 1% of the oxide originally present in the batch: Na_2O (added as sulphate) 0·06%, K_2O (added as carbonate) 0·12%, B_2O_3 0·15%, ZnO 0·04%, PbO (up to 50% PbO) 0·014%. The loss of B_2O_3 in melting is well known. When this is added as H_3BO_3 the loss is liable to be greater than when borax is used.

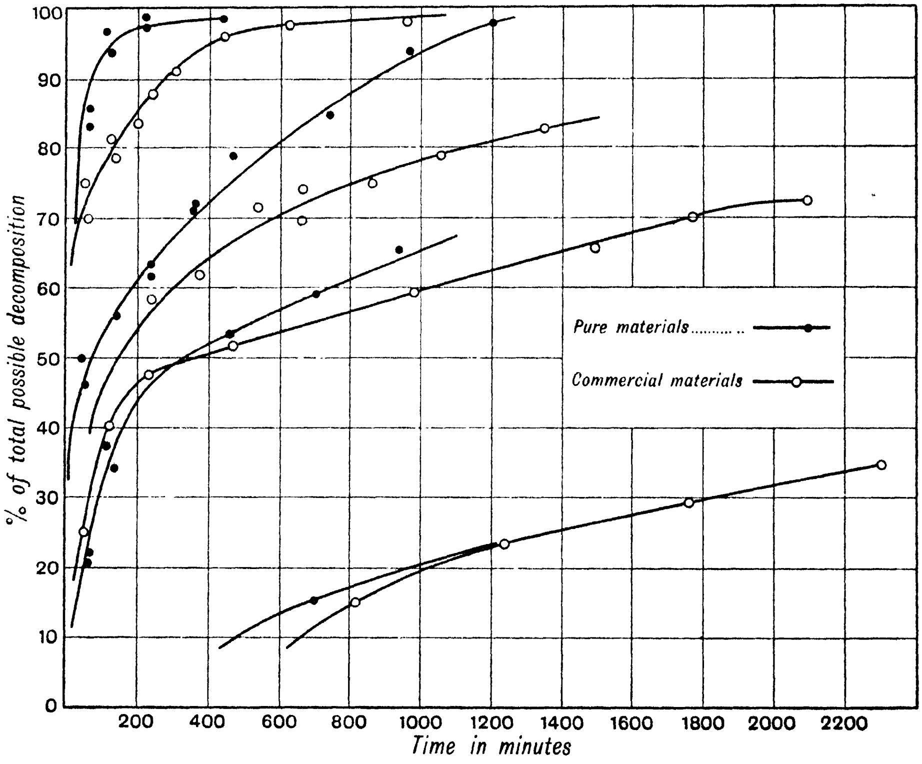


Fig. 15.—Rate of Reaction of Batch Mixture to give Glass of Percentage Composition SiO_2 75, Na_2O 15, CaO 10.

Progress of Reaction.—For a silica–calcium carbonate–sodium carbonate mixture, G. Tammann and W. Oelsen (Z. anorg. Chem. 1930, **193**, 245) state that loss of CO_2 begins at 600° with a heating rate of 10° per minute, and is complete at 860°. Up to 750–775° the main decomposition, beginning as low as 500°, is of calcium carbonate, after which sodium carbonate reacts with silica. Fig. 15 (from J. T. Howarth, F. R. R. Sykes and W. E. S. Turner, J. Soc. Glass Tech. 1934, **18**, 295) shows the behaviour of the batch to give the glass SiO_2 75, Na_2O 15, CaO 10 made up (*a*) from 150–180 I.M.M. mesh quartz grains, similar calcite ones and sodium carbonate; (*b*) from materials of good commercial quality as used in pot melting. Fine grain size increases the rate of decomposition. The more silica present in the batch the slower is the rate of melting, not only because silica dissolves slowly in any case, but the increase in silica content makes the glass more viscous and slows up the solution rate still more. Tammann and Oelsen state that the sequence of reaction in their mixture was as below:

Temperature.	Reaction.
600–830°	$CaNa_2(CO_3)_2 + 2SiO_2 \rightarrow Na_2SiO_3 + CaSiO_3 + 2CO_2$
720–900°	$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$
780°	Eutectic $Na_2CO_3 + Na_2Ca(CO_3)_2$
813°	M.p. $Na_2Ca(CO_3)_2$
855°	M.p. Na_2CO_3
912°	$CaCO_3 \rightarrow CaO + CO_2$ ($p = 760$ mm.)
960°	$Na_2Ca(CO_3)_2 \rightarrow CaO + Na_2O + 2CO_2$
1,010°	$CaO + SiO_2 \rightarrow CaSiO_3$

With a red lead–potassium carbonate–silica mixture studied by the same workers the sequence was given as:

Temperature.	Reaction.
600°	$Pb_3O_4 \rightarrow 3PbO + O$
670–730°	$PbO + SiO_2 \rightarrow PbSiO_3$
750°	$K_2CO_3 + SiO_2 \rightarrow K_2SiO_3 + CO_2$

At 835° the lead silicate dissolved in potassium carbonate although molten lead oxide did not mix with the latter.

Sintering or Fritting Temperature.—W. E. S. Turner and co-workers have determined the temperatures at which mixtures cohered. For the $x SiO_2$–CaO–Na_2O-mixtures (x=6 and 4) fritting took place in 5–10 minutes at 800° or at 750° in several hours, the $4SiO_2$ mixture needing a slightly higher temperature than that of the $6SiO_2$ to give the same degree of cohesion.

Later Stages of Melting.—At higher temperatures the $4SiO_2$ mixture melted to a mass free from solid particles (batch free) at 1,100°, whilst the $6SiO_2$ was not quite free at 1,200°. The rate of melting of a batch depends on its composition, *i.e.* on the specific batch materials as well as on the composition of the glass which it is to produce. Batches containing alumina are liable to produce a refractory scum on the surface of the molten glass, whilst the same amount of alumina added as felspar is less liable to cause trouble. Silica scum is sometimes found on the top of tank-melted glass if the melting temperature is not very high and all the alkali is added as soda ash, whereas the inclusion of a little saltcake helps to prevent this. Grain size and the amount of moisture present also affect the melting rate.

Refining.—The melting of an ordinary soda–lime–silica glass results in the liberation of approximately 15% of the batch weight as gas. This has a marked effect on the melting rate by promoting mixing of unmelted constituents which might otherwise segregate. The use of all-burnt lime in some U.S.A. batches has been criticised on account of their low "volatile" content. Much gas remains in the form of bubbles called "seed" or "boil" according to size when the glass has become free from batch. The removal of this may be facilitated in two ways, (*a*) by reducing the viscosity either by increasing the temperature or by batch additions such as borax, salt cake, ammonium salts, *e.g.* the sulphate, fluorides (*see* Fig. 16, due to H. Jebsen-Marwedel, which shows the velocity of rise of a bubble through a window-glass melt in relation to its size and the temperature of the glass), or (*b*) adding to the melt when most of the seed has been removed some volatile substance that creates an upward rush of large bubbles which collect the finer ones so that when the turbulence subsides the glass soon becomes seed-free or "plain." Such agents are lump "arsenic" (As_2O_3) or ammonium nitrate for best quality pot-melted glasses, a potato or water-soaked wooden block about 4 × 4 × 2 in. stuck on an iron rod for ordinary pot glasses, and a common wet banana stalk for tank melted glasses. The work of F. Gelstharp and S. R. Scholes (J. Ind. Eng. Chem. 1912, **4**, 16; Trans. Amer. Ceram. Soc. 1913, **15**, 585), Allen and Zies in U.S.A. (J. Amer. Ceram. Soc. 1918, **1**, 787), and W. E. S. Turner and co-workers in this country (J. Soc. Glass Tech. 1926, **10**, 3, 20; 1927, **11**, 65, 190, 205) showed that arsenious oxide added to the batch could not act as a refining agent by reason of its volatility as had been widely believed, because most of the arsenic so added remained in the glass partly as As_2O_3 and partly as As_2O_5, their ratio being on the average 0·45:1 for the glass of percentage composition SiO_2 75·8, CaO 9·6, Na_2O 14·4 whilst the loss varied irregularly between 0–14·8% of the total added as that quantity varied from 1–10 parts per 1,000 sand in the batch (Allen and Zies found for commercial glasses losses of 11–33%). Turner (*l.c.*) found no evidence that arsenious oxide acted as a flux in soda–lime–silica glasses though it did for potash–lead oxide–silica glasses. When used with nitre in the batch, a definite increase in rate of refining is obtained.

Cullet.—The proportion of waste glass or "cullet" returned for remelting varies with the process, and some small firms making containers use little else. In general the cullet used comprises 25–45% of the total material melted for bottle manufacture, 55–60% for electric lamp bulbs and 50–75% for lead crystal. Melting is assisted by its inclusion, but above 60% it appears to retard the rate of refining of soda-lime glasses (F. W. Hodkin, H. W. Howes and W. E. S. Turner, *ibid.* 1929, **13**, 25) although this is not the case with potash-lead oxide glasses (S. English, G. A. Green, F. W. Hodkin and W. E. S. Turner, *ibid.* 1929, **13**, 37). Careful laboratory experiments have shown that provided the cullet and batch are mixed and melted to produce a homogeneous glass there are no differences in physical properties which cannot be explained by differences in chemical composition even when cullet was remelted nine times (V. Dimbleby, H. W. Howes, W. E. S. Turner and F. Winks, *ibid.* 1929, **13**, 304). As used in works practice, however, the size of the cullet and its chemical composition is such that complete homogeneity cannot be reached during melting. This does lead to irregular physical properties, particularly brittleness, and for this reason it is good practice to crush all cullet used to a size depending on the type of ware being made.

Moisture in the batch gives improved melting when in small amount (*c.* 1–2% for soda ash, 4% for saltcake or potash–lead oxide glasses) and seems to improve the refining of saltcake glasses. If present to the extent of more than 5%, the glass tends to become viscous through inhomogeneity.

Decolorising.—All "colourless" glasses contain some iron oxide which gives them a more or less pronounced bluish or yellowish-green tint if no steps are taken to counteract the effect. If the total iron expressed as Fe_2O_3 does not exceed approximately 0·09%, it may be masked by the addition of "decolorisers" to the batch. These act either *chemically* by oxidising the iron largely to the ferric condition, the colour being then less noticeable, or *physically* by giving to the glass a complementary tint so that, although the light transmission of the glass is lowered and it thereby appears slightly duller, it has no definite colour. Chemical decolorisers are nitrates, manganese and cerium dioxides, arsenious oxide, which is always, and especially with nitrates in the batch, converted partly to arsenic oxide which can give up oxygen if necessary at a late stage of the melting process to keep the iron oxidised, whilst among the physical decolorisers are manganese dioxide, nickel and cobalt oxides and selenium. Chemical methods alone cannot deal with more than 0·03–0·04% Fe_2O_3. With higher amounts a residual tint remains that can only be suppressed by use of a physical decoloriser. In pot melting from best quality materials very little decoloriser is needed, less than 0·2 parts MnO_2 per 1,000 sand with 1–2 parts As_2O_3 being enough for lead crystal glass. With a potash glass, nickel oxide may be used, but with soda glasses a brown and not a pink tint is given which is more intense than that given by manganese, and the amount required is only $\frac{1}{50}$–$\frac{1}{100}$ of the MnO_2 If cerium oxide is employed, then it is claimed that much less physical decoloriser is needed. Nickel is preferred to manganese, where it can be used, since it is not so sensitive to the furnace atmosphere, for when reducing gases are present the pink tint imparted by manganese fades and may turn to a green which makes the colour worse than ever. In the slightly reducing conditions that prevail in tank furnaces the best decoloriser is undoubtedly selenium with cobalt oxide to give full colour compensation. Arsenic is also added, the amounts generally employed per 1,000 lb. sand are 0·4–0·7 oz. Se, $\frac{1}{12}$–$\frac{1}{20}$ that amount of cobalt oxide or the equivalent of "powder blue," and 1–3 lb. As_2O_3. Much research on the behaviour of selenium has shown that it can give rise to colours from (*a*) elementary Se (pink), (*b*) polyselenides (brown), whilst selenides, selenites and selenates gave no colour. The importance of furnace atmosphere and of batch composition (oxidising or reducing constituents) was made clear by W. Höfler (Glastech. Ber. 1934, **12**, 117, *also* with A. Dietzel, *ibid.*, p. 297). It has been shown that carbonaceous matter in a sand may, if not too large in amount, actually improve the decolorising action of selenium, but that too much produces the brown selenium coloration. If only very slightly in excess, the use of a small amount of nitre will restore the balance.

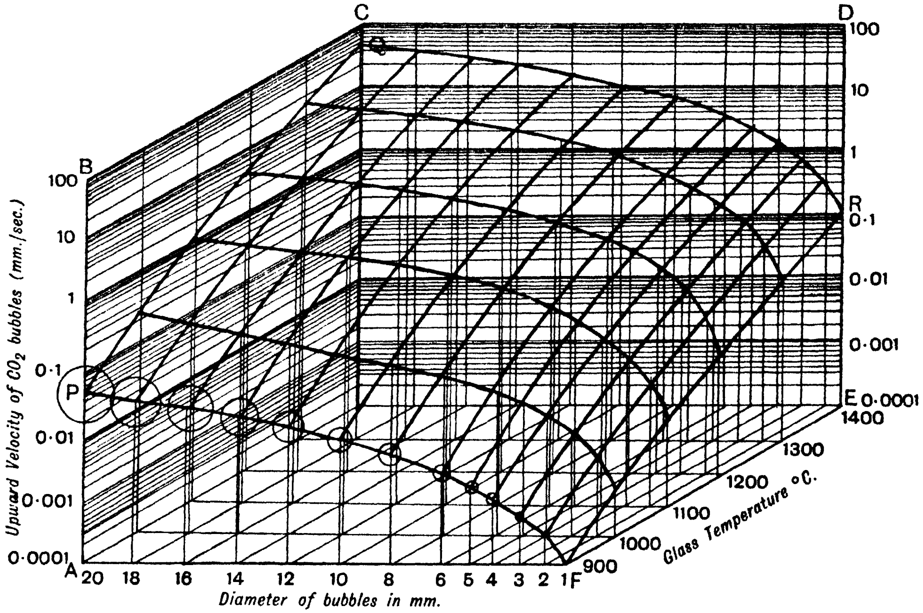


FIG. 16.

Devitrification.—In cooling down the 150–200° between melting and working temperatures and even more in standing at the lower temperatures obtaining in such parts of furnaces feeding automatic machinery as feeder channels and sheet glass drawing chambers, the glass is liable to "devitrify," that is crystalline material separates from solution. The same effect may take place at the sidewalls or on the bottom of the furnace or in any place where the temperature remains continuously lower than the liquidus temperature of the composition. In general the fewer the glass components the easier it is for devitrification to occur.

The tendency of a glass to devitrify may be directly determined experimentally by heating a small specimen at a definite temperature for a time long enough to permit the establishment of equilibrium condition and then cooling quickly ("quenching") to preserve any crystals that may have developed. This method has been applied with conspicuous success by the American Geophysical Laboratory investigators, notably by G. W. Morey and co-workers, to the drawing up of equilibrium diagrams showing the stability relationship of the various crystalline phases that may separate from glasses. An alternative method of study is to heat a specimen in a shallow boat of platinum in a furnace having a fairly steep temperature gradient along the length of the boat. After attaining equilibrium conditions the boat is removed, cooled and the nature and disposition of any crystal forms determined, their position in the boat being correlated with the furnace temperature-gradient (G. Tammann, Z. anorg. Chem. 1914, **87**, 248; J. F. Ponomarev, J. Soc. Glass Tech. 1927, **11**, T39; W. B. Silverman, *ibid.* 1937, **21**, T118; E. Preston, *ibid.* 1940, **24**, T101, 139). Equilibrium diagrams as presented in two dimensions usually show either (*a*) freezing-point data for the various compounds, (*b*) isotherms in the various "fields" or (*c*) boundary curves and tie-lines. The complete representation of the relationships in a three-component system such as Na_2O—CaO—SiO_2 is only possible by a solid figure and the diagrams mentioned are merely various sections of this figure. Fig. 17 shows the boundary curves and tie lines, *i.e.* the composition of the various compounds and the fields containing the liquid compositions within which they may exist in equilibrium, for the $Na_2O{\cdot}SiO_2$—$CaO{\cdot}SiO_2$—SiO_2 part of the Na_2O—CaO—SiO_2 system, according to G. W. Morey and N. L. Bowen (*ibid.* 1925, **9**, 226). In this region of the system there are seven

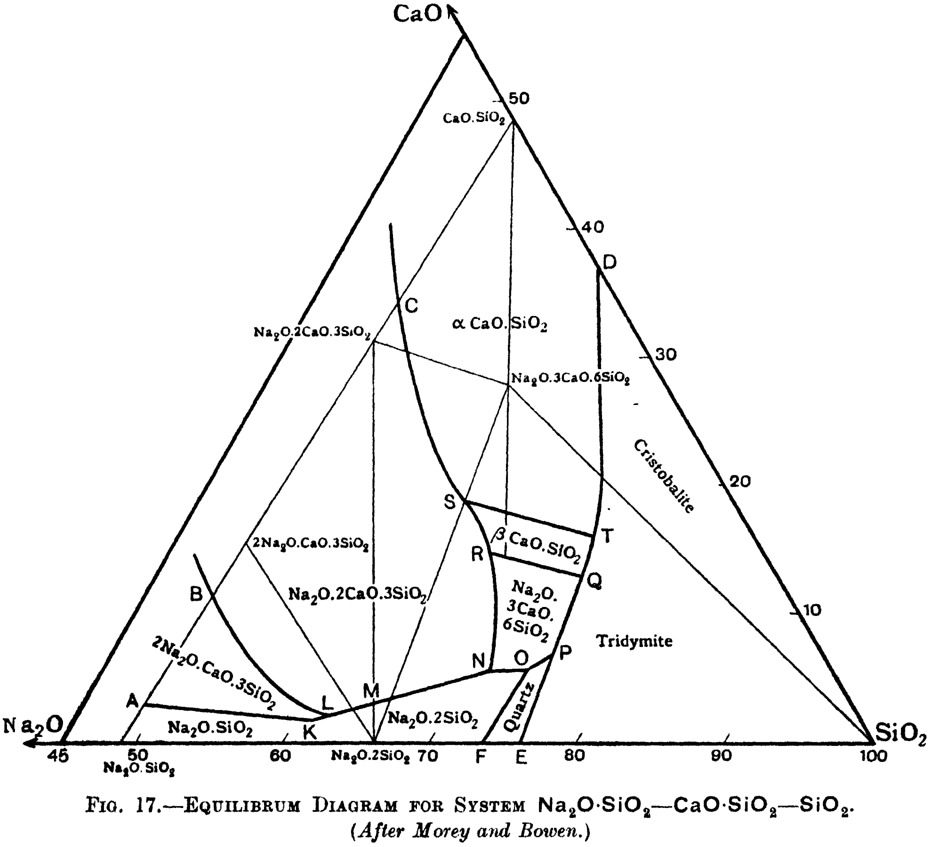


FIG. 17.—EQUILIBRUM DIAGRAM FOR SYSTEM $Na_2O{\cdot}SiO_2$—$CaO{\cdot}SiO_2$—SiO_2.
(*After Morey and Bowen.*)

compounds, namely SiO_2 (as quartz, tridymite and cristobalite), $CaO{\cdot}SiO_2$ (in two modifications, wollastonite and pseudo-wollastonite), $Na_2O{\cdot}SiO_2$, $Na_2O{\cdot}2SiO_2$, $2Na_2O{\cdot}CaO{\cdot}3SiO_2$, $Na_2O{\cdot}2CaO{\cdot}3SiO_2$ and $Na_2O{\cdot}3CaO{\cdot}6SiO_2$ (devitrite). The last named is a frequent separation when commercial bottle glass devitrifies.

Fig. 18 shows a portion of the data for the system K_2O—CaO—SiO_2 according to G. W. Morey, F. C. Kracek and N. L. Bowen (*ibid.* 1930, **14**, T162), and some properties of a number of important crystalline compounds that may occur in glasses are reproduced in the table given on the next page.

For further references to work on this subject, *see* the following: Na_2O—SiO_2, G. W. Morey and N. L. Bowen (J. Phys. Chem. 1924, **28**, 1167); F. C. Kracek (*ibid.* 1930, **34**, 1583). K_2O—SiO_2, F. C. Kracek, N. L. Bowen and G. W. Morey (*ibid.* 1937, **41**, 1183). CaO—SiO_2, N. L. Bowen, J. F. Schairer and E. Posnjak (Amer. J. Sci. 1933, **26**, 193). PbO—SiO_2, R. F. Geller, A. S. Creamer and E. N. Bunting (J. Res. Nat. Bur. Stand. 1934, **13**, 237). Li_2O—SiO_2, F. C. Kracek (J. Phys. Chem. 1930, **34**, 2641). Na_2O—B_2O_3, G. W. Morey and H. E. Merwin (J. Amer. Chem. Soc. 1936, **58**, 2248). PbO—B_2O_3, R. F. Geller and E. N. Bunting (J. Res. Nat. Bur. Stand. 1937, **18**, 585). K_2O—PbO—SiO_2, R. F. Geller and E. N. Bunting (*ibid.* 1936, **17**, 277).

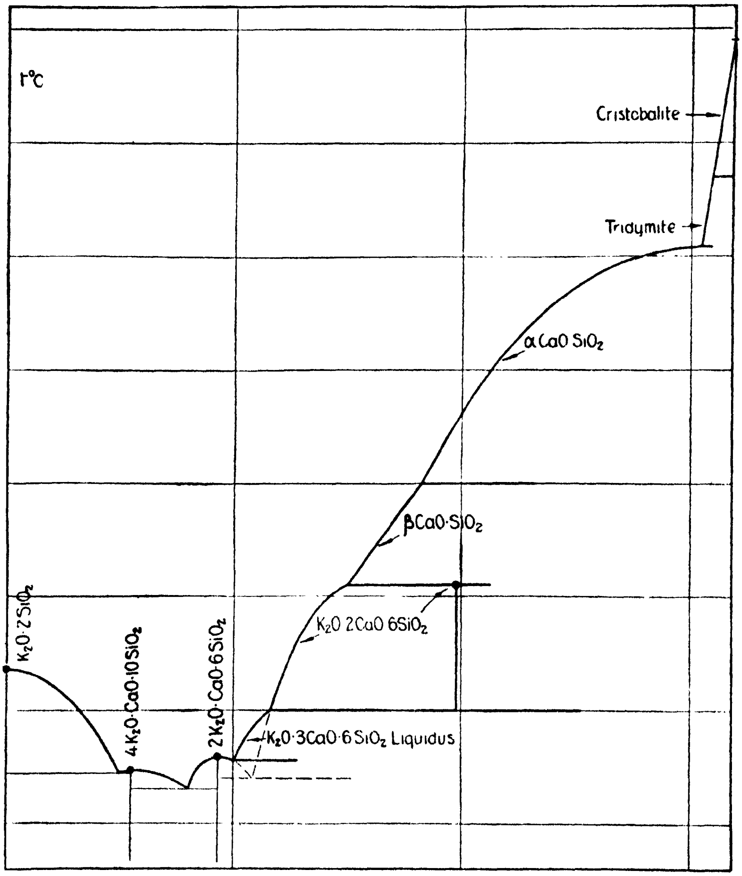


FIG. 18.

Na_2O—MgO—CaO—SiO_2

(partial), G. W. Morey (J. Soc. Glass Tech. 1936, **20**, 245; J. Amer. Ceram. Soc. 1930, **13**, 714). Na_2O—CaO—SiO_2—B_2O_3 (partial), G. W. Morey (*ibid.* 1932, **15**, 457).

Na_2O—CaO—Al_2O_3—SiO_2,

G. W. Morey (*ibid.* 1930, **13**, 718). **Sheet Glass**, E. Preston (J. Soc. Glass Tech. 1940, **24**, 139).

Morey showed that when Al_2O_3 replaced CaO in the parent glass,

$1{\cdot}11Na_2O{\cdot}0{\cdot}95CaO{\cdot}6SiO_2$, PROPERTIES OF CRYSTALLINE COMPOUNDS (AFTER MOREY).

Compound.	Melting temp. °C., reaction temp. (*r*) or inversion temp. (*i*).	Crystal habit.	Crystal system.	2V.	Optical character.	Refractive indices.				
						α	ω	β	ε	γ
SiO_2 low quartz	573*i*	Bipyramides.	Hexagonal.		unix.+		1·544		1·553	
SiO_2 high quartz	870*i*									
SiO_2 low tridymite	1,470*i*	Plates.	Pseudo-hexagonal.	35°	biax.+	1·473		1·47		1·469
SiO_2 low cristobalite	1,713	Plates.	Pseudo-cubic.		uniax.−		1·487		1·484	
$Na_2O·SiO_2$	1,089	Needles.	Orthorhombic.	large	biax.−	1·513		1·520		1·528
$Na_2O·2SiO_2$	874	Plates, needles.	Orthorhombic.	50–55°	biax.−	1·497				1·508
$K_2O·SiO_2$	976	Granular.	Orthorhombic.	35°	biax.+	1·520				1·528
$K_2O·2SiO_2$	1,045	Plates.	Orthorhombic.	large	biax.−	1·503				1·513
$K_2O·4SiO_2$	770	Plates.	Mono- or triclinic.	large	biax.+	1·477				1·482
$\beta CaO·SiO_2$	1,150*i*	Needles.	Monoclinic.	39°	biax.−	1·616		1·629		1·631
$\alpha CaO·SiO_2$	1,540	Hexagonal plates.	Hexagonal.		uniax.+		1·610		1·654	
$PbO·SiO_2$	764	Prisms.	Monoclinic.	65°	biax.−	1·947		1·961		1·968
$2PbO·SiO_2$	743		?	80°	biax.−	2·13		2·15		2·18
α-$4PbO·SiO_2$	725*r*	Irregular plates.	?	40°	biax.+	2·31		2·34		2·38
$2Na_2O·CaO·3SiO_2$	1,141*r*	Octahedra.	Isometric.					*n*=1·571		
$Na_2O·2CaO·3SiO_2$	1,284	Equant.	?			1·595				1·598
$Na_2O·3CaO·6SiO_2$	1,060*r*	Prisms.	Orthorhombic.	75°	biax.+	1·564		1·570		1·579
$K_2O·CaO·SiO_2$	1,630		Hexagonal.		uniax.+		1·600		1·605	
$2K_2O·CaO·3SiO_2$	1005*r*	Octahedra.	Pseudo-cubic.					*n*=1·572		
$\beta K_2O·3CaO·6SiO_2$	1020*i*	Needles, plates.	Orthorhombic.		biax.−	1·56				1·57
$\alpha K_2O·3CaO·6SiO_2$	1115*r*	Prisms.	Orthorhombic.	large	biax.+	1·575				1·59
$2K_2O·CaO·6SiO_2$	959	Plates.	Mono- or tri-clinic.		biax.−	1·540				1·544
$4K_2O·CaO·10SiO_2$	946	Plates.	Hexagonal.		uniax.−		1·548		1·537	
$K_2O·2CaO·9SiO_2$	1,050*r*	Prisms, plates.	Mono- or tri-clinic.	large	biax.−	1·515				1·535
$K_2O·2PbO·2SiO_2$	918				uniax.−		1·93		1·72	
$K_2O·4PbO·8SiO$	779					1·69				1·79
$K_2O·PbO·4SiO$	757			75°	biax.+	1·590		1·612		1·650
$2K_2O·PbO·3Si$	735*r*				biax.+	1·685				1·665

CENTRAL

it lowered the liquidus temperature from 1,075° to 997° at 2% Al_2O_3 by weight, further additions raised the temperature to a maximum of 1,028° at 8% addition, the minimum of approximately 1,000° was reached at 11·5% after which further increase in Al_2O_3 raised the temperature. The primary phase separating was tridymite up to 2% addition, devitrite ($Na_2O{\cdot}3CaO{\cdot}6SiO_2$) 2–8%, wollastonite ($\beta$-$CaO{\cdot}SiO_2$) 8–17%. In another series where Al_2O_3 was added to the same parent glass instead of substituting CaO, a similar but not so large drop in the liquidus temperature was brought about by 2% addition. Addition of 2·4% MgO to a similar parent glass was shown by Morey (*l.c.*) to produce the striking drop of 200° in liquidus temperature, the separating phase becoming devitrite instead of tridymite. With larger additions the liquidus temperature rises again and the separating phase becomes diopside,

$$CaO{\cdot}MgO{\cdot}2SiO_2,$$

which crystallises readily. The effect of MgO and Al_2O_3 in thus lowering the liquidus temperature of soda–lime–silica glasses makes them useful additions to reduce the tendency of such glasses to devitrify. The soda–magnesia–lime–silica glass used for electric lamp bulbs and the addition of alumina to batches for producing tubing, bottle, optical and resistance glasses are examples of such practice. Magnesia is rarely used in amount greater than 2·5–3% and the use of Al_2O_3 is rarely above 4–5%.

Substitution of part of Na_2O by K_2O is frequently beneficial. It is dangerous to make general statements, however, as a small change in composition may move the glass into another field with liquidus temperature higher rather than lower that of the original.

Alumina is a very important constituent of opal glasses, most of which may be regarded as special cases of devitrification. The nature of the opacity may be controlled to a great extent by the amount of Al_2O_3 present, thus, with none at all, fluorides may produce no opacity, with 4–6% a good opal, and with higher amounts only a slight opacity. Small amounts of chlorides and sulphates also modify the type of crystal separation.

E. Zschimmer and A. Dietzel (Sprechsaal, 1929, **62**, 506, 543, 562, 584, 603, 619, 638, 657; J. Soc. Glass Tech. 1929, **13**, Abs. Nos. 404, 612) with co-workers determined the maximum crystallisation velocities and temperatures at which this occurs for a number of types of glass. They state that for

$$Na_2O{-}CaO{-}SiO_2$$

glasses the least devitrification tendency occurs when the sum of the Na_2O and CaO contents is approximately 26%. W. Hänlein (Z. tech. Physik. 1933, **14**, 418) has studied the behaviour of the SiO_2—CaO—Na_2O—K_2O glasses. For lead oxide glasses with constant PbO the effect of variations in SiO_2 and K_2O is shown by W. Hirsch (Glastech. Ber. 1932, **10**, 625) in the following table (*see also* R. Geppert and A. Dietzel, Sprechsaal, 1934, **67**, 591):

K_2O.	PbO.	SiO_2.	Temperature of maximum crystallisation velocity.	Temperature at which glass and crystal in equilibrium.	Maximum crystalisation velocity (V. max.).
			°C.	°C.	
6·08	33·14	60·42	1,370	1,405 ± 5	79·5 μ/min.
8·07	33·07	58·60	1,200	1,325	30·7 ,,
10·16	33·04	56·63	1,050	1,225	3·51 ,,
12·16	33·04	54·55	850	1,050	6·0 μ/hour.
14·03	33·09	52·62	700	860	2·0 ,,

The Manufacture of Different Types of Glassware.

The manipulation of glass and its formation into articles of glassware can be carried out entirely by hand, but machinery has almost entirely displaced hand labour in the manufacture of the common types of glassware capable of being produced in bulk to a standard pattern. In practically all cases the molten glass in the furnace is taken and shaped straightway into the articles required. Two exceptional cases are: (1) the manufacture of better-class optical-glass lenses and prisms, where the pot of glass is allowed to cool down slowly and the cold pieces of glass form the basis of further working; (2) the lampworking or bench-glass blowing industry, the raw material for which consists of glass tubing or rod previously made at the furnace.

Manipulation by Hand.—The processes and tools used are numerous; two or three of them are common to almost every operation, some others are also of very general use. Thus, gathering glass on a blowpipe and marvering it or shaping it in a shaping block are the usual initial stages in making any glass object.

Fig. 19 depicts several of the more essential tools, such as the tongs, shears, callipers, and flattening boards. The blowpipe is an iron tube about 4 ft. 6 in. long and ⅝–1 in. external diameter, has a rounded end for mouth-piece and a "thickened nose," usually slightly trumpet-shaped, on the end of which glass is gathered by dipping into and rotating in the molten glass. The *marver* is a polished iron plate on which the gathered mass is rolled on the end of the blowpipe until it attains a cylindrical form, called the *parison*, either hollow or solid, the hollow form being obtained by blowing down the pipe. The glassmaker's chair seen in Fig. 22 has projecting arms on which the blowpipe is rolled backwards and forwards in order that the spinning or rotating shall preserve the rounded outline of the vessel. At this chair sits the master workman, or glassmaker, who finishes the article by means of various tools in conjunction with rotation of the pipe.

The various types of hand operation may be classified as (1) free hand work, involving gathering, marvering, blowing and drawing as in making glass tubing; (2) turned work, or chair work, involving, possibly, all the preceding processes together with the use of tools; (3) mould-blown work, in which the marvered gathering is blown out in a mould—bottles, electric lamp bulbs, beakers and flasks; (4) combined mould and turned work. This last is now common. Nowadays the bowl of a wine glass is frequently blown in a mould and the stem and foot added at the chair. Although at least 40 years old this is still known as "New Process" in the Stourbridge trade.

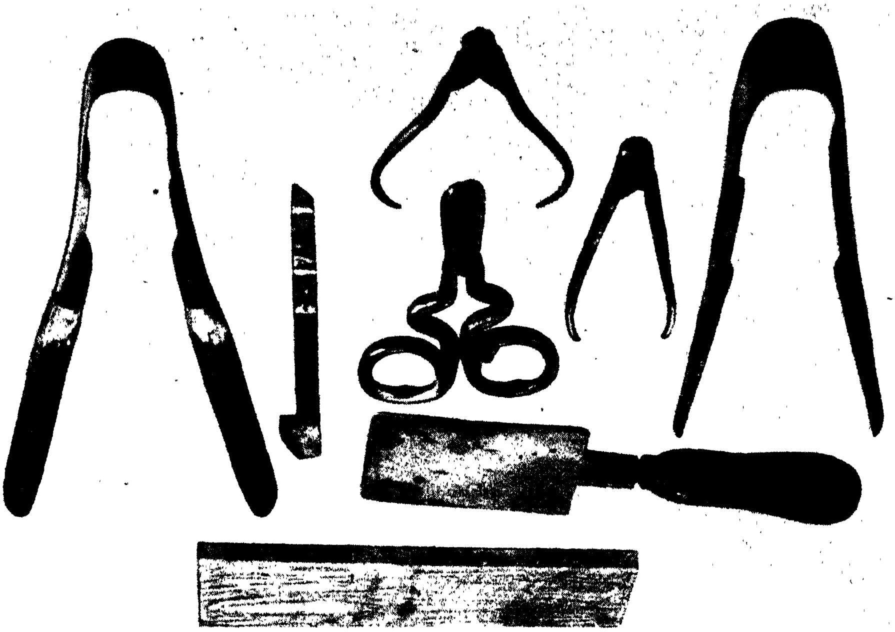


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FIG. 19.—TOOLS FOR HAND MANIPULATION.

The diagrams (Fig. 20) serve to illustrate the operation of producing the hand-made tumbler, that is, an example of turned work. A very small quantity of glass is gathered on the end of the blowpipe and blown out into a small bulb (*a*). This in turn serves as the centre round which a further gathering (*b*) is made, sufficient for the size of the tumbler on order. By blowing down the pipe and also rotating the mass of glass in a shaping block, the shape (*c*) is obtained, the constriction being made so that eventually the fully blown vessels can be detached readily. By swinging the iron slightly, and by the further use of the shaping block, the parison is given a slightly conical shape (*d*), after which, by blowing and swinging, shape (*e*) is obtained, and finally (*f*), after the somewhat thicker bottom has been flattened out by contact with a flat and perfectly smooth iron plate. The pipe is detached by drawing a tool across the constricted part of the shoulder while the vessel is still hot and then giving the pipe a slight tap at its extreme end. The tumbler, with adhering shoulder, is now given its final form in one of two ways. This may be done at the chair by placing the bottom of the tumbler in a holder, reheating the shoulder in the mouth of the furnace, and cutting it away by means of shears. The glass-

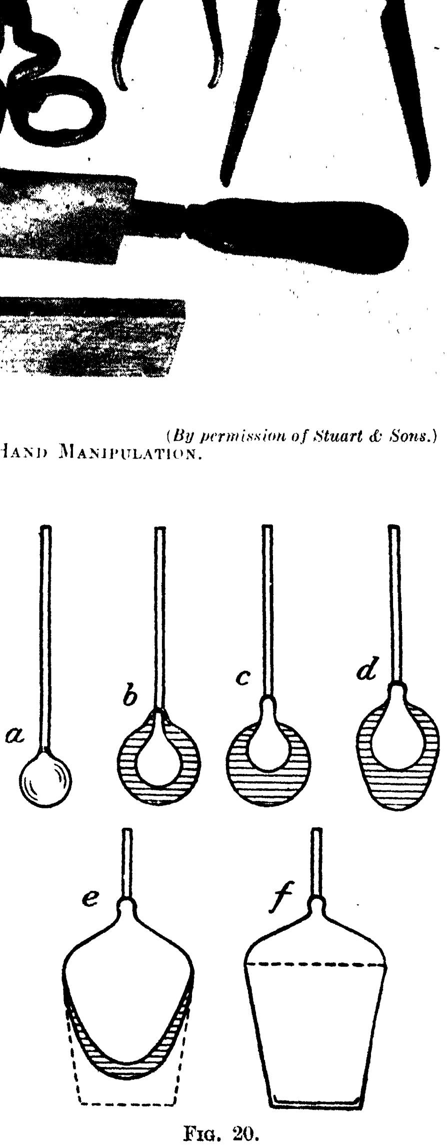

FIG. 20.

maker then finally rotates the cylinder on the arms of the chair, and by means of tongs rounds off the lip. The second process of finishing is described under "Edge Melting and Cracking off Machines," in the section dealing with cold working processes (p. 602).

The manipulation of glass on the pipe is further illustrated by Figs. 21 and 22.

In the case of mould-blown glassware, the gathering of glass after being marvered and formed into the parison, is blown out into a mould corresponding to the external size of the article required. The moulds may be of wood, carbon, brass or iron. Moulds of special alloys have also been tried. The moulds of wood and carbon produce the best finish, whilst the iron moulds are less satisfactory from this point of view, although their durability causes them to be used in the majority of cases. Where exceedingly good finish and high wear-resistance is needed nickel chrome steels have given very good results, *e.g.* for press moulds. Metal moulds may be used dry or may be covered with some form of lubricant, usually a paste, in which case the moulds are referred to as paste moulds. The paste is frequently a mixture of finely-divided carbon, such as lamp black or red lead and well boiled linseed oil, but other forms of paste are in use. The paste must be thinly and uniformly spread, and the moulds after each blowing operation are dipped into water to cool them and prevent the paste being burned away too rapidly. Electric lamp bulbs, chimneys, blown tumblers, beakers and flasks are blown in paste moulds.

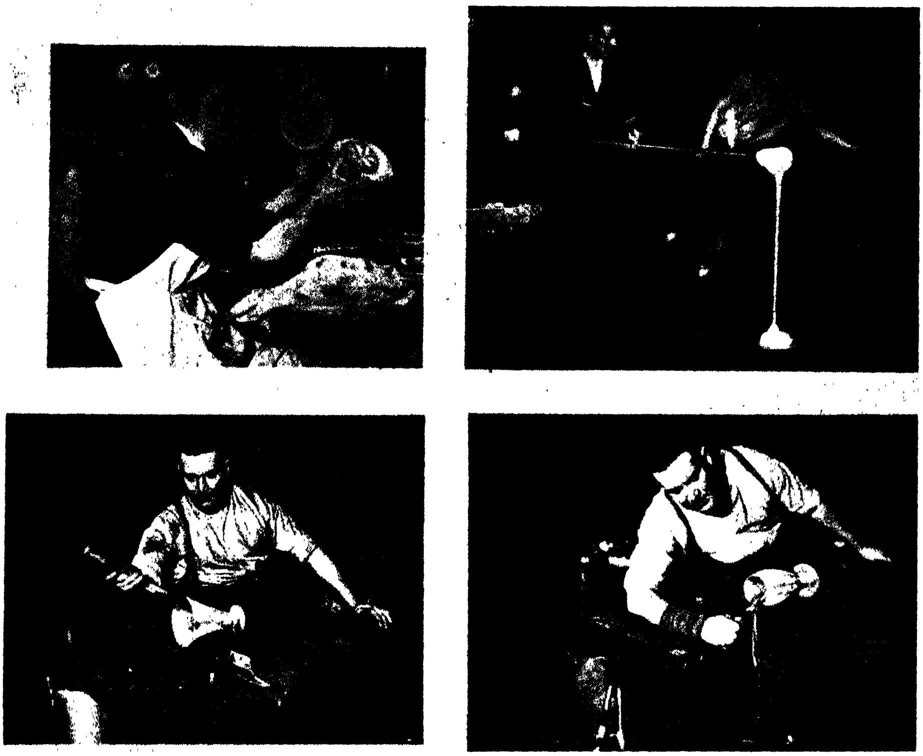

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FIG. 21.—HAND WORKING.

Hand-made bottles are almost invariably blown in dry moulds. The process involves gathering at the end of the pipe, marvering into the parison, which usually has a somewhat smaller diameter at the end adjacent to the pipe than at the free end, swinging slightly to cause elongation, and then blowing out into the mould. Two methods of finishing the bottle are used according to the thickness of the neck. In heavy bottles with a thickened neck the latter is made at the furnace by the bottle maker, who adds an additional ribbon to the neck where it has been broken off from the pipe, and then by rotating the bottle at the chair and inserting a neck-forming tool the neck is given its final shape. In lighter made bottles, such as those used for medicines, the end which has been burst off from the blowing iron, is softened in a small subsidiary furnace known as a glory hole, usually heated by town gas or oil, and the neck is formed by pressing back the softened portion of the glass by means of the neck-forming tool. Very few bottles are now hand made, the process being almost completely replaced by mechanical methods.

Chemical, Scientific and Heat-Resisting Glassware.—Almost all types of this particular class are made by hand. Flasks and beakers are blown in paste moulds. Fig. 23 shows a mould for a flask, and Fig. 24 the initial form of a beaker, the shoulder is cut off by the second process described in connection with the tumbler (p. 602), and the edges are heated and flanged and a lip added where desired.

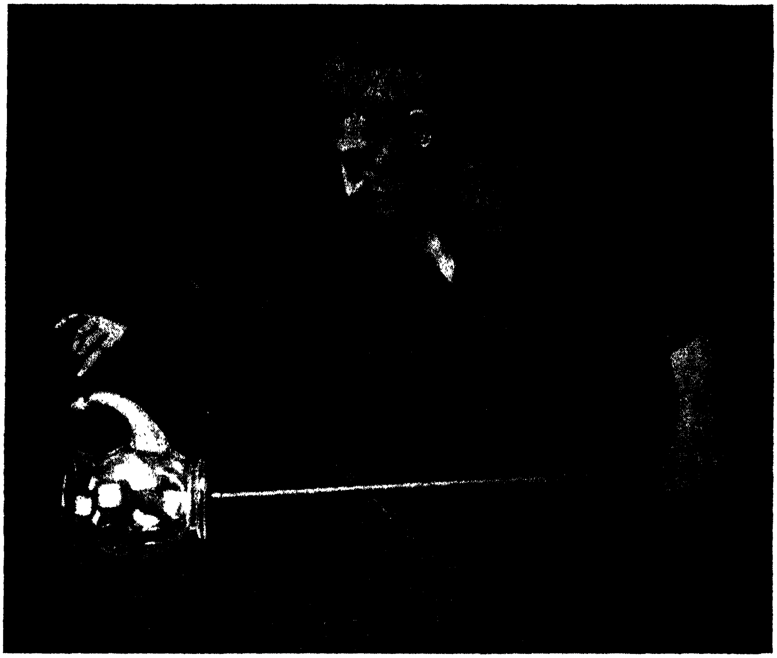

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FIG. 22.—HAND WORKING.

Glass Tubing is drawn by hand by first marvering a thick hollow cylinder of glass, built up by several gatherings, and then lowering this cylinder in a vertical position until its base unites with a disc of hot and soft glass, attached to a holder held by another operator. When the union is firm, the assistant with the holder walks backwards along a wooden track crossed by strips of wood, pulling out the glass tubing as he walks, the chief glass blower at the same time turning his blowpipe to and fro and occasionally blowing down it to prevent the walls of the glass from collapsing. The tubing is laid on the wooden strips and after cooling

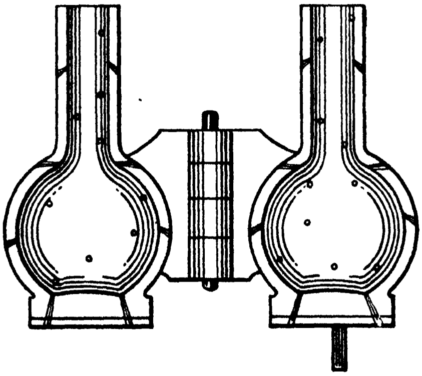

FIG. 23.

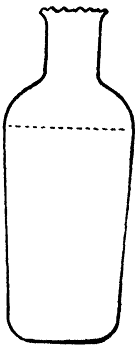

FIG. 24.

cut into lengths. Most tubing is now made by automatic machinery described later.

Glassmaking Machines.

The following general types may be distinguished according to the type of glass and the process involved.

CONTAINER AND DOMESTIC WARE.

(1) **Pressing Machines**, producing dishes, jars, plates, lenses, bowls, common heavy tumblers by the pressure of a plunger on glass contained in a mould of suitable design. Where the article must be of precise dimensions it is customary to provide an overflow portion or "font" to accommodate excess glass and frequently the pressure is exerted by the plunger acting on the glass in this font portion. Fig. 25 shows a simple type of press. The table and plunger rod must be rigid enough to resist deformation, and, particularly in automatic working, adequate cooling should be provided. This is usually effected by air-blast on the moulds and water cooling inside the press plunger.

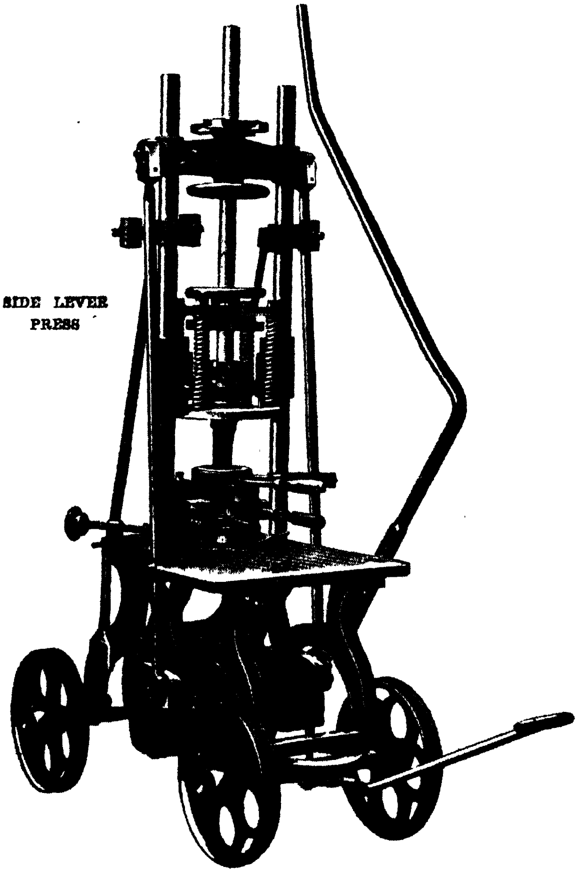

FIG. 25.

(2) **Blowing Machines**, which can be subdivided again according to the way in which they carry out the two distinct stages of formation through which practically all hollow ware passes, namely formation of the parison and blowing the parison to the final shape. Parison formation may be carried out by pressing, blowing, or suction, whereas in nearly all cases, final shaping is accomplished by blowing, though one type of Roirant Machine uses suction for this purpose. Consequently, the machines are known as:

(*a*) *Press and Blow Machines*, used to make wide-mouth ware, such as jam and pickle jars, milk bottles of certain types. Miller, Mitchell and the Hartford Milk Bottle machines are examples of this type worked in conjunction with feeding devices.

(*b*) *Blow and Blow Machines*, to which belong the narrow-neck container-forming machines that are charged by gravity feeders. In this type of machine the charge or " gob " of glass is dropped into the parison mould which has no bottom and is held in the inverted position, *i.e.* neck portion down to receive the gob. The latter is then " blown down " around the small plug set within the neck mould to form a depression from which blowing may start, the plug is withdrawn, a " baffle plate " is seated on the mould and compressed air is admitted around the plug to blow up the glass to the baffle plate, so forming a bottle with the neck of proper size but with a body smaller and walls thicker than the finished article. This is the parison, and the mould is then " reverted " or turned right way up, and the main portion opened leaving the parison hanging in the neck mould by which it is transferred to the blow mould where it is blown to the final shape. Early machines carried out these blowing operations at definite stations, the moulds being fixed to an intermittently rotating table or tables. Fig. 26 shows such a machine by O'Neill, this particular model being fed by hand and not from a feeding device. The parison mould at the charging station is shown at P, transfer station at TR, and a parison mould partially inverted at M on its way back to the charging station. A blow mould open after discharging the bottle shown at the right is seen at F approaching the transfer station. The compressed air cylinder C and the piston rack drive to the machine R are seen below the mould tables. In its to- and fro-motion the rack bar R tripped valves controlling the supply of compressed air to key positions and so timed the operation of the machine, which indexed on one station each to- and fro-cycle of the rack bar. In more modern types of machine much of the pneumatic cylinder operation has been replaced by cam mechanisms, and in the Lynch No. 10 each movement of the piston is operative so that only half the compressed air is used. This type also provides means for carrying out the blowing whilst the machine is moving instead of only at the " dwell " positions, thus giving much more control of blowing time and reducing the time of dwell at each station, a most important improvement.

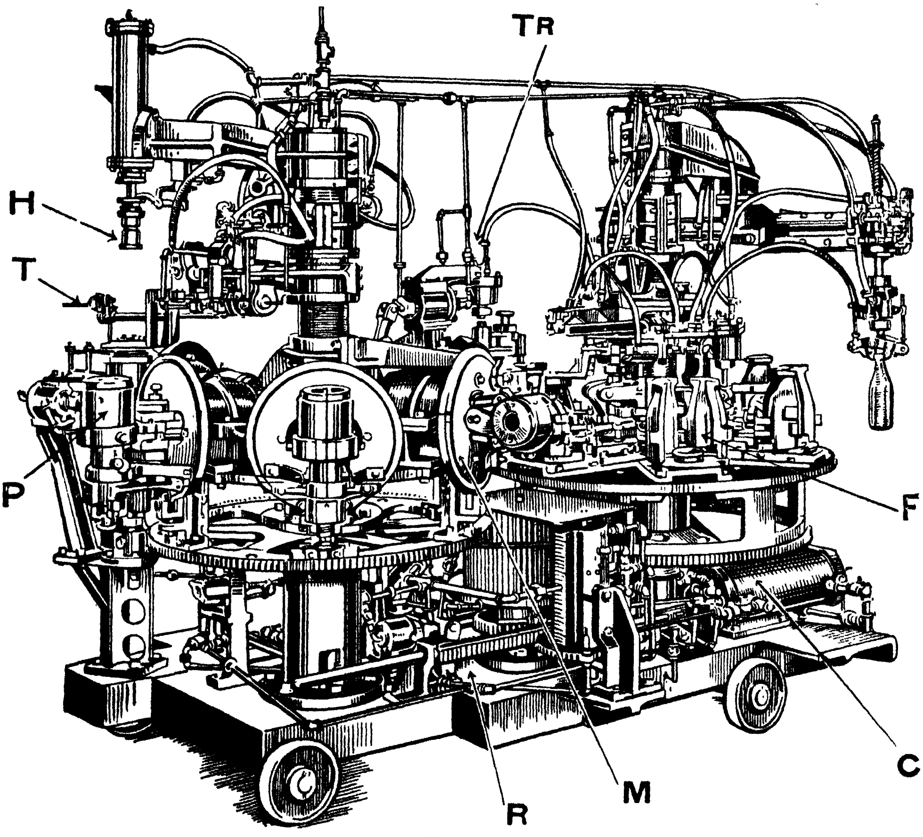

FIG. 26.

Another blow and blow machine is the Hartford " I.S." This is usually assembled in sets of four units, each of which may be making ware different from its neighbours, a feeder discharging gobs of the appropriate weight in predetermined order. This type is very successful in making small high-class containers such as scent and pharmaceutical bottles, but is by no means confined to such work.

(*c*) *Suck and Blow Machines* form the parison by suction, and as the mould cavity is filled with glass this method gives close control of the amount gathered and hence produces ware of constant capacity. Since the moulds actually touch the molten glass in gathering, temperature conditions are severe and moulds need frequent cleaning and repair. As the mould is raised from the glass a knife cuts off the tail of excess glass and throws it back into the forehearth. The knife rests below the gathering orifice for a short time until just before the mould opens and then frequently a slight puff of air is blown around the neck plug to form a starting cavity for the final blowing. This also has the effect of expelling a little hot glass through the gathering orifice to reheat the chilled portion that has been in contact with the knife. The parison is then transferred to the blow mould and blown to the finished shape.

The first of such machines to work successfully was the 6 arm type constructed by Michael J. Owens, an Irishman in America, and 10 and even 15 arm machines were later developed. Fig. 27 shows a 15 arm Owens machine and Fig. 28 is a diagrammatic view of one unit or arm of the machine. A revolving pot, Fig. 29, 8–10 ft. diameter and only a few inches deep fed by a stream of glass from the main melting-furnace serves as the pool from which the suction moulds gather, thus ensuring that each successive mould gathers fresh thermally-homogeneous glass and that each sheared tail cut off by the knife is reheated and blended with the glass in the pot before another gather is taken from that particular spot. This pot needs a special housing and heating burners and is a decidedly expensive device to run, consequently later inventors devised alternatives in the form of stationary forehearths built on to the sides of the working ends of the furnaces. These in general are not so satisfactory but with care can be used successfully. The later suction machines too are smaller than the Owens which had such a large production as to make it unsuitable for the execution of small orders (using triple moulds, more than 200 small bottles a minute can be made). Thus, the O'Neill suction machine (Fig. 30) is a twin table machine having 3, 4 or 6 sets of moulds, the Monish Fig. 31 has 3 sets and the Roirant only one set, though a later type of Roirant has six sets. The single Roirant machine actually sends its suction mould C into the furnace to gather the glass (Fig. 32). With these smaller machines a much more varied output may be produced since several can be operated from one furnace, each making a different class of ware. A more constant load may also be kept on the furnace with such an arrangement.

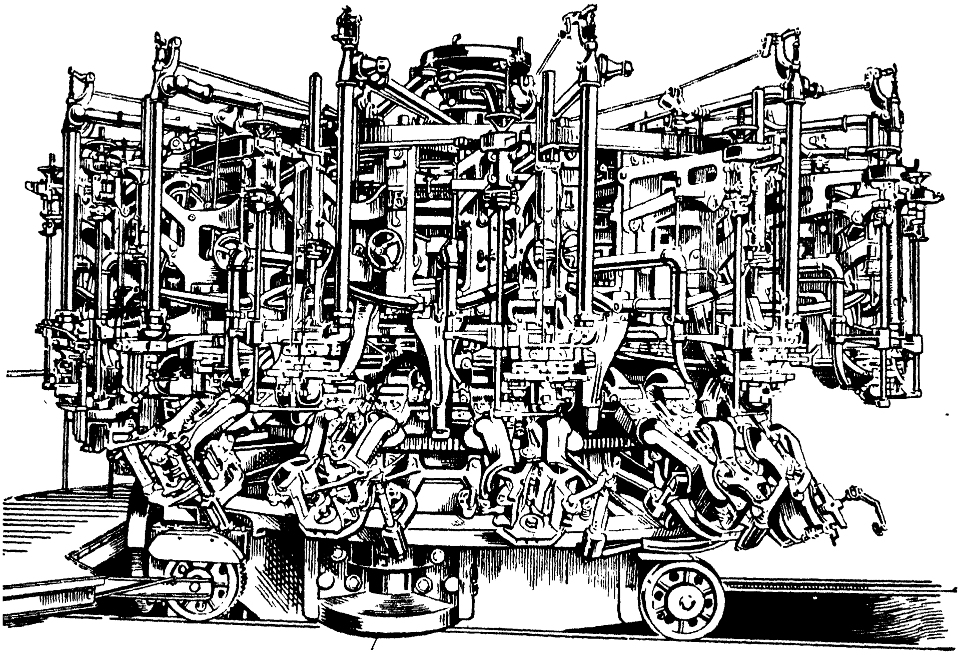

FIG. 27.

The suction machines so far mentioned are used for making container glassware, but a similar principle is used in those of the Westlake type (B.P. 26222, 26225/11, 397425) (Westlake, Ivanhoe, Ohio) making electric lamp bulb, cylindrical thermos flask and tumbler blanks. A " ram " is reciprocated in and out of

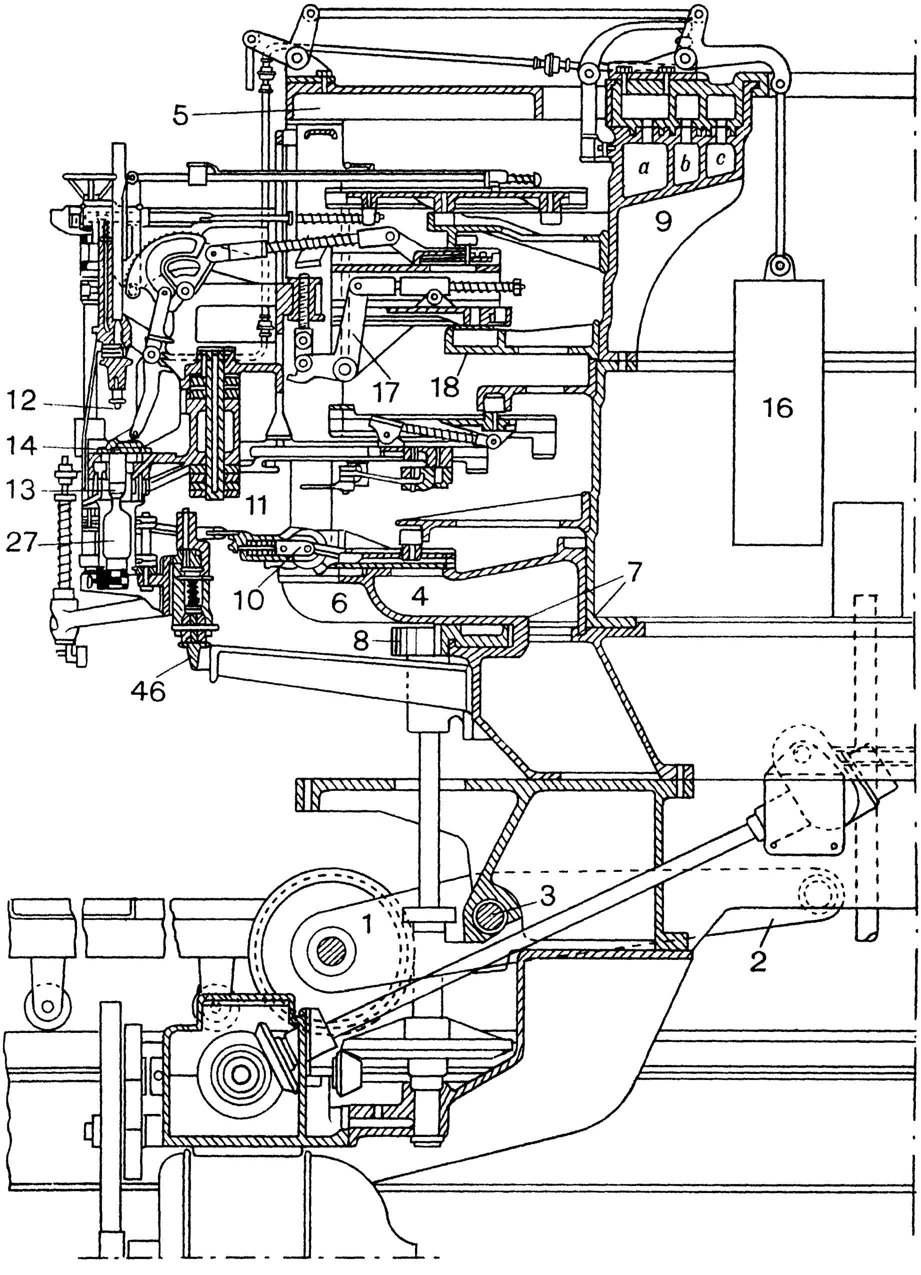

FIG. 28.—PART SECTION OF OWENS MACHINE UNIT.

a "gathering boot" built on to a tank furnace, and gathers two or more charges of glass in small suction moulds. These it drops on to upturned blowpipes where they are secured by hinged clamps which engage flanges on the glass and the blowpipes, rotating, go through the motions of a glass blower giving puffs of air to blow up the masses to form a parison and turning through 180° to allow these to elongate sufficiently by the time the blow moulds close around them for the final blowing to shape. Paste moulds are used for these machines, and during the idle part of their cycle they are dipped in water or suds. A more recent development of lamp bulb machines is the Corning No. 399 (B.P. 276,606, 1927), Fig. 33. A stream of glass issuing from a feeder is formed by rolls into a thin ribbon having thickened lumps spaced regularly along it. These, as the ribbon moves on horizontal guides, register over openings below which are located rotating moulds carried on an endless belt. Above the ribbon another endless belt carries blowheads which register above the moulds, and, when the still hot glass has sagged through the apertures, come down and blow it out into the moulds. Further along the track the blow heads lift, the moulds open and then the depending

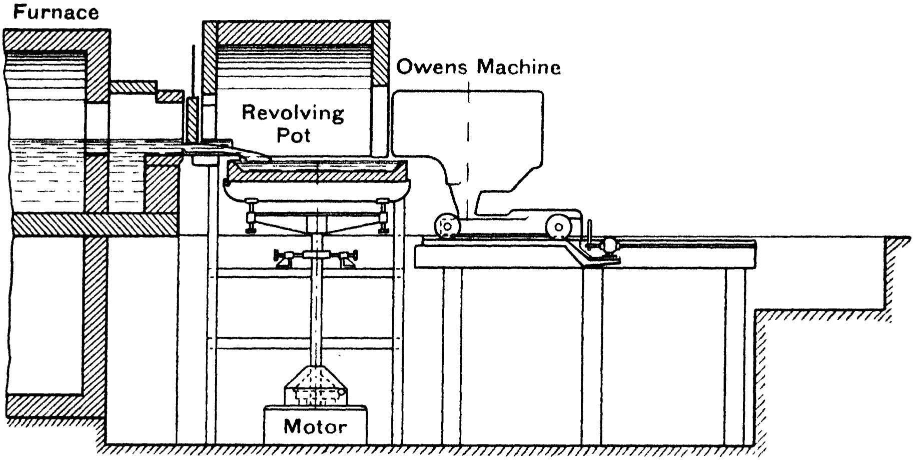

Fig. 29.—Lay-out of Owens Machine Plant (diagrammatic).

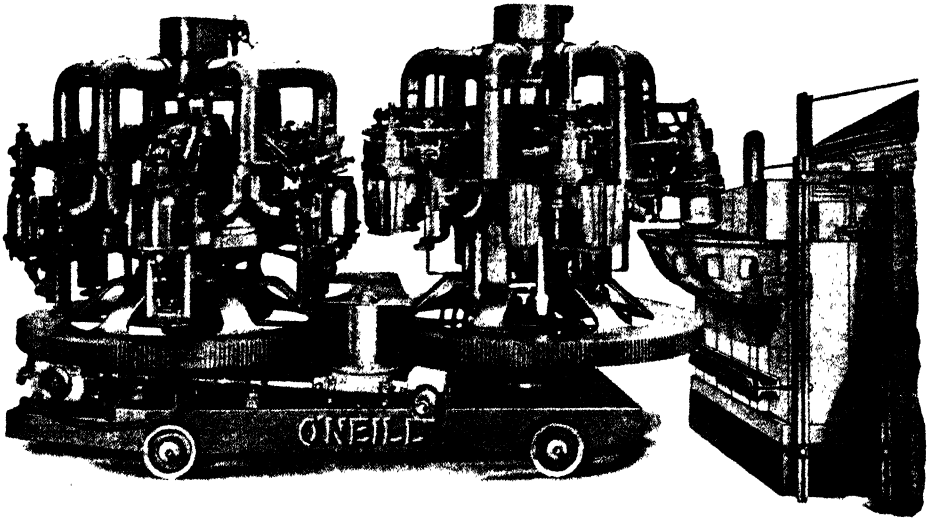

Fig. 30.—The O'Neill Vacuum Machine in Position against the O'Neill Patented Forehearth.

bulbs are stripped off the glass ribbon, being fed to an annealing lehr whilst the ribbon goes to the cullet chute.

The Westlake machine with 24 spindles makes 90,000–95,000 bulbs per day, the Ohio with 48 spindles makes over 100,000, whilst the Corning machine makes 300,000–400,000 per day, and so far has not been used in Britain. Such productiveness has probably prevented the commercial development of several other patented machines for making bulbs.

Feeding Devices.—The term generally refers to a channel extending from the working end of a tank furnace, from which it can be cut off by a damper or "gate," to a narrowed rounded nose some 4–8 ft. from the furnace wall. The floor of the channel often rises towards the nose as shown in Fig. 34 as this slope permits glass contaminated by contact with the refractory walls to drain to a sump away from the orifice in the bottom of the feeder through which glass is discharged under gravity. This discharge may be (rarely) continuous or (more usually) interrupted under the action of (*a*) a reciprocating refractory plunger 5 working just above the orifice 4, or (*b*) alternate pressure and vacuum applied to a "bell" of refractory material above the orifice. In the latter case the bell itself may be reciprocated also. The mechanical type is commonest,

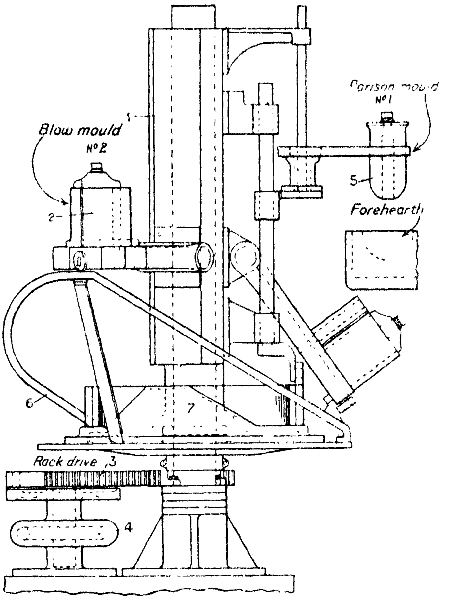

FIG. 31.—MONISH SUCTION MACHINE.

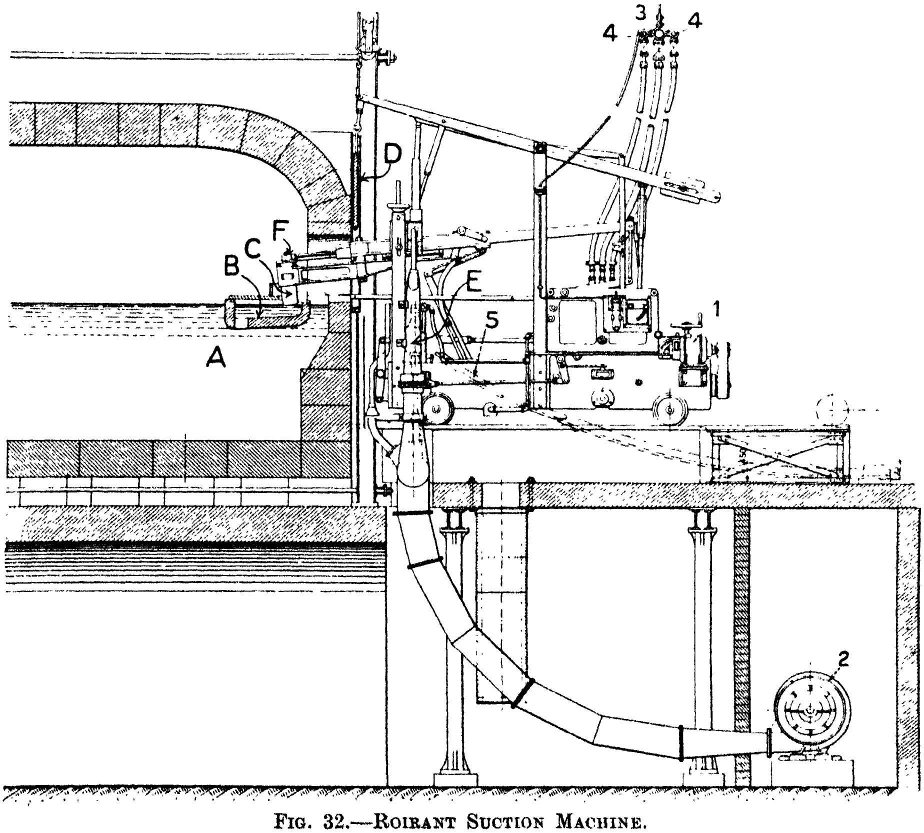

FIG. 32.—ROIRANT SUCTION MACHINE.

and the orifice diameter is adjusted between the general limits of ¾–2 in. by insertion of easily replaceable fireclay bushings in order to control the weight discharged. The height of the plunger end above the orifice also affects the discharge, whilst the speed of descent and ascent as well as the shape of the plunger end, controls the general shape of the "gob" of glass discharged. Rapid descent gives short fat gobs and slow descent long thin ones, whilst rapid ascent gives the pronounced "neck" on the issuing stream. This serves to reduce wear on the shears used to cut the glass into separate charges and also to minimise the amount of glass chilled by the shear blades.

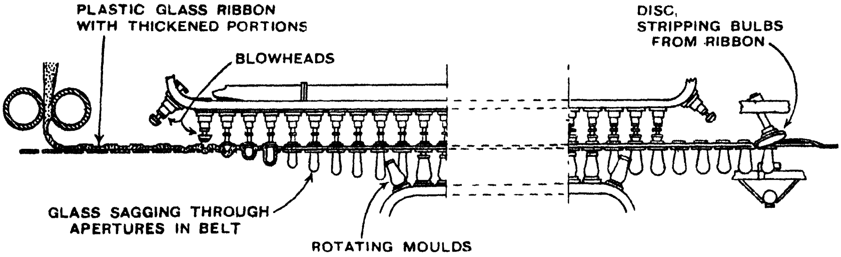
PLASTIC GLASS RIBBON WITH THICKENED PORTIONS
BLOWHEADS
DISC, STRIPPING BULBS FROM RIBBON
GLASS SAGGING THROUGH APERTURES IN BELT
ROTATING MOULDS

Fig. 33.—Corning No. 399 Damp Bulb Machine.

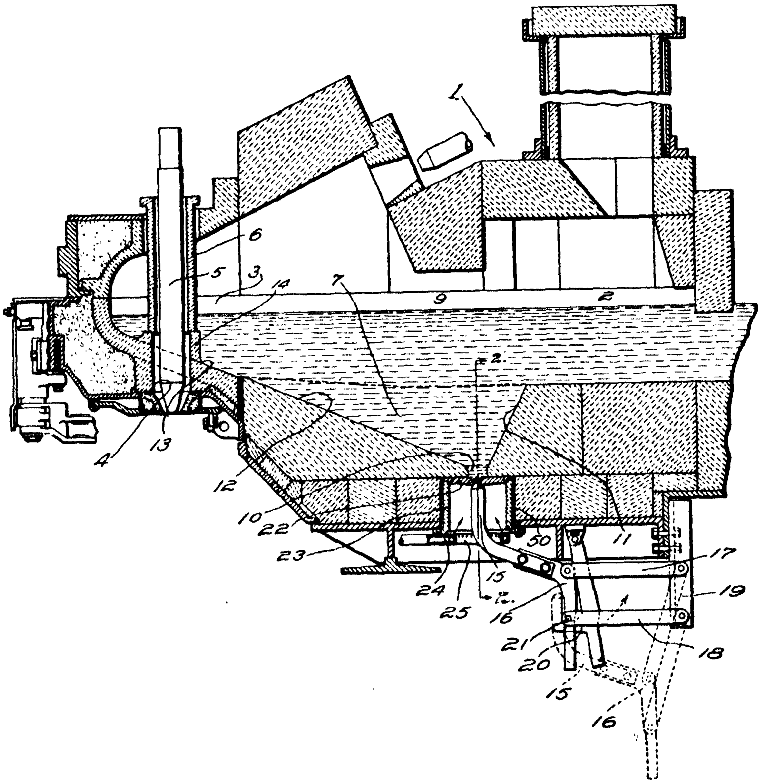

Fig. 34.—Sectional View of Glass-Feeding Device.

Suction-fed forming machines gather their own glass from a pool which may be a revolving pot as in the Owens type or a much smaller affair largely housed under the furnace crown as in the Roirant "A.6" type. Annular instead of saucer-like troughs have also been patented. Many machines gather from stationary forehearths or boots built on to the working end of the furnace. The Monish, O'Neill, Pearson and

Mitchell machines do this, whilst the Roirant, Westlake and Ohio machines gather from a boot inside the furnace or from the furnace itself.

(3) **Drawing Machines** are used to produce window glass on the one hand and tubing or rod on the other.

(*a*) *Tube Drawing.*—The first and most widely used process is that of E. Danner (B.P. 110642, 111521 both of 29 November, 1916; U.S.P. 1218598, 1219709, 1220201 (all of 1917). In this, glass melted either in a tank or pot furnace is transferred to a special pot 1, Fig. 35, provided with a discharge spout feeding glass into a trough 3, the glass level in which is kept constant by means of an indicating device 4, 5, 6. The trough is divided into three compartments by bridges which hold back surface impurities from the glass passing through, the flow is controlled by the gate 8 and the glass escapes over a lip 9 on to the mandrel in the form of a ribbon. The mandrel comprises a tube 11 of nickel-chrome alloy on which is mounted a sleeve 13 of refractory material provided with a nichrome nose 14. The mandrel is housed in a muffle heated by a gas burner to a controlled temperature and is rotated by gearing so that the stream of glass from the trough is wrapped round it and the inclination of the mandrel (12–18°) causes the glass to flow down to the tip from which it is drawn off as tube or rod (" cane "). In the former case air under pressure is supplied to the other end of the mandrel and the size and wall thickness produced depend on the amount of glass fed per unit time, the air pressure and the rate of drawing. Between the mandrel and the drawing machine is a tube run of 100–180 ft. consisting of a series of grooved pulleys, sometimes asbestos lined, spaced very closely near the mandrel and about 30 in. apart near the drawing machine. Part of this may be covered to control the rate of cooling in the critical region. The drawing machine consists of two caterpillar endless belts faced with asbestos, between which the tube or rod is fed. The top belt is adjustable to take various sizes of product and is spring loaded to give a grip on the work. The rate of pull can be varied from 16 to 900 ft. per minute. At high speeds the work is cut into 4–5 ft. lengths by a revolving vane arrangement which just breaks each length roughly, but for larger work the cut is made truly by wet carborundum stones, travelling at the same speed as the tube and acting in conjunction with a device to apply a breaking moment. The cut lengths are then fed to a gauging machine which moves them one at a time over a series of gaps, increasing in size until the glass falls through one of them. The production of the Danner machine is indicated in Table XI.

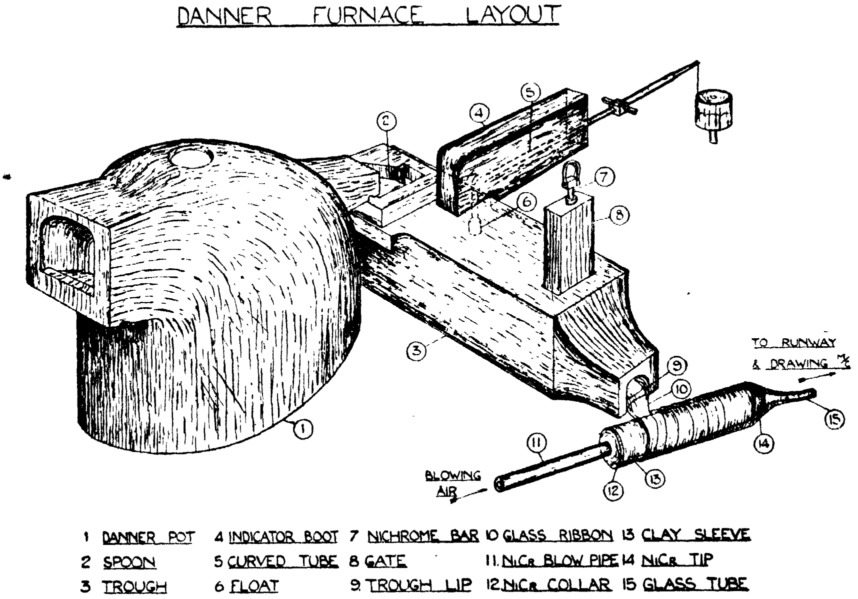

Fig. 35.—Danner Tube-Drawing Machine.

In contrast with this side-drawing process there is the W. J. Woods (B.P. 354509; U.S.P. 1829429) process of vertical drawing which has been applied to the production of thermometer tubing with a white stripe backing the bore. Glass from the main supply 26, Fig. 36, controlled by the gate 32 is drawn up from the nozzle 30 supplied with air under pressure by pipe 31, 39 and the white enamel for the stripe is introduced from container 34 by nozzle 35 at a point which can be controlled by adjustment of the position of the container 34. L. Sanchez-Vello, B.P. 349315, has a process in which the tube starts vertically downwards (Fig. 37) from an annular orifice between an aperture

TABLE XI.—PRODUCTION, ETC., OF TUBE AND ROD ON DANNER MACHINE.[1]

	Diam. (mm.).	Wall (mm.).	Rate of drawing, ft. per min.	Un-gauged lb./min.	% of product to size.	Blowing pressure in W.G.	Temperatures, °C.		
							Pot.	Ribbon.	Muffle.
30% PbO glass.	3·25–3·75	Rod	280–300	5·5	70	nil.	1,080	1,040	900
	2–2·5	0·4–0·5	820–840	6	70	0·01	1,100	1,070	800
	4·5–5·5	0·7–0·85	300–320	6·25	75	0·1	1,100	1,075	860
	6·5–7·5	0·9–1·1	180–200	6·5	80	0·6	1,110	1,090	950
	10·5–12	0·86–1·02	120–130	7·5	85	1·2	1,110	1,090	950
	17·5–19·5	1·5–1·75	44–48	7·5	90	1·6	1,110	1,095	900
	24–26	0·6–0·7	68–72	7·0	90	7·0	1,140	1,120	960
	40–45	1·0–1·25	22–23	7·5	95	18·0	1,140	1,125	990
Lampworking glass (18·5% Na_2O).	5–6	0·75–1·0	165	3·5	95	0·2	1,120	1,080	1,000
	11–12	1–1·25	50	3·75	95	0·5	1,120	1,080	1,000
	26–28	1–1·25	30	5	80	6·7	1,110	1,070	1,000
	31–33	1–1·25	33	6	80	5·7	1,110	1,070	950
Mercury Resistant soda-lime glass.	7–8	0·8–1·0	110	3·5	95	0·02	1,110	1,080	990
	14–15	1–1·25	45	3·75	95	0·6	1,120	1,080	1,000
	20–22	1–1·25	38	4·5	95	1·5	1,120	1,080	1,000
	37–39	1–1·25	20	5·5	70	8·3	1,110	1,085	980
Yellow opalescent tubing glass.	9–10	1–1·25	80	3·5	95	0·4	1,180	1,110	1,040
	19–21	1–1·25	30	4·25	85	1·07	1,180	1,110	1,040

in a forehearth bottom and a rotating hollow mandrel with a flared end over which the glass stream flows. The tube is actually drawn off by a side-pulling device located some distance from the forehearth and special means are provided for altering that distance to suit the drawing. After cutting into lengths the latter are delivered on to a conveyor band feeding on to an inclined plane so that the tube is kept gently rolling until cool enough to put into store.

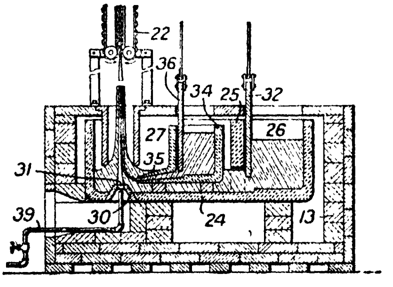

FIG. 36.—MAKING STRIPED THERMOMETER TUBING BY W. J. WOOD'S PROCESS.

All the above are continuous processes, but there are discontinuous ones in which preformed annular glass blanks are threaded one after the other on a mandrel located in a furnace so that they soften and fuse together to form a thick walled tube which is drawn off to suitable size from the lower end of the mandrel. Such a process is patented by P. Blum and P. A. Favre (B.P. 300646, 304664). The advantage is that the blanks may be made at any time and stored, and that quick changes of glass type can be made. Usually, however, to economise heat the blanks are taken straight from the press to be threaded on the mandrel whilst hot.

(*b*) *Window Glass Drawing.*—The processes fall into the following classes:

(i) *Vertical Drawing* as in the Fourcault and Pittsburgh processes. In that due to E. Fourcault (B.P. 28790, 1903; F.P. 338146, 1904; G.P. 161279, 178579, 178580, 182829; 185839 and many later), first operated in 1914 at Dampremy, a debiteuse, Figs. 38 and 39, consisting of a shallow fireclay boat with a slit running along the bottom is held submerged in the glass in the drawing chamber A, Fig. 40, fed with glass which in its passage from the melting end of the furnace has been skimmed free of surface impurities by the floating bridges shown stretching across from either side. A thin ribbon of glass is thus extruded from the slit and this is caused to freeze round a " bait " consisting of a metal bar studded with nails and carried by a wire screen which is drawn by the asbestos covered rolls until the glass sheet itself can be engaged by the latter and used to provide the grip. The rolls do little more than remove the glass ribbon as it is formed, and this in conjunction with the debiteuse overcomes the tendency of surface tension to cause a narrowing of the sheet leading to failure. It was this difficulty which prevented much earlier processes of an Englishman, W. Clarke in 1857 (B.P. 489, 1857) and of Parish and Frank in 1881 and 1883 from being successfully operated. Cooling " canisters " of metal through which fluid is circulated are disposed on either side of the sheet immediately above the floor of the debiteuse so that the glass temperature is brought down from 1,040°C. in the drawing chamber to about 650°

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[1] V. E. Sibilia, J. Soc. Glass Tech. 1939, **23**, T292.

when leaving the debiteuse and on reaching the first pair of rollers is about 500° so that the sheet can be gripped without deformation. As the greatest danger of fracture is experienced around 460°, this temperature must be kept above the first pair of rollers at any rate, so that the drawing may go on without having resort to the bait again should a fracture occur. The rollers are located in the "drawing shaft" which forms a rough and ready kind of annealing tunnel. and by the twelfth pair the temperature has dropped to about 125°. Shortly afterwards the ribbon of glass emerges on to the top floor of the building, where it is cut into sheets and taken to store after immersion in a dilute acid tank to remove surface alkali. To give relief against crushing pressure in the event of irregularities in the sheet, one of each pair of rolls is carried on a bell crank lever with a loading weight capable of adjusting the pressure at which the roll lifts away from the sheet. These levers may be seen at the right of Fig. 39 whilst the motor drive to the other members of each pair is shown in Fig. 38. The range of thickness of such glass is 2–10 mm., and some of the thicker material may be used for making ground and polished plate or for automobile windscreens without grinding and polishing. The difficulty in making thick glass is that the temperature and rate of drawing are so low that devitrification in and round the debiteuse, always a danger, becomes serious. Much prestige was lost to this process for a time because in order to obtain "sweet" working conditions the glass was made with a high alkali content, but this has not been the case for many years and modern compositions run around SiO_2 72–73, Al_2O_3 and Fe_2O_3 0·5, CaO 9·5–10·5, MgO 1·5–3, Na_2O 13·5–15%.

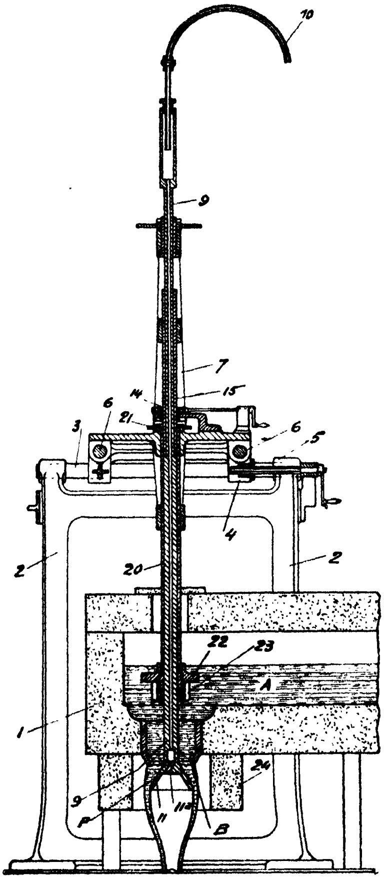


Fig. 37.—Downward Drawing of Tubing by L. S.-Vello Process.

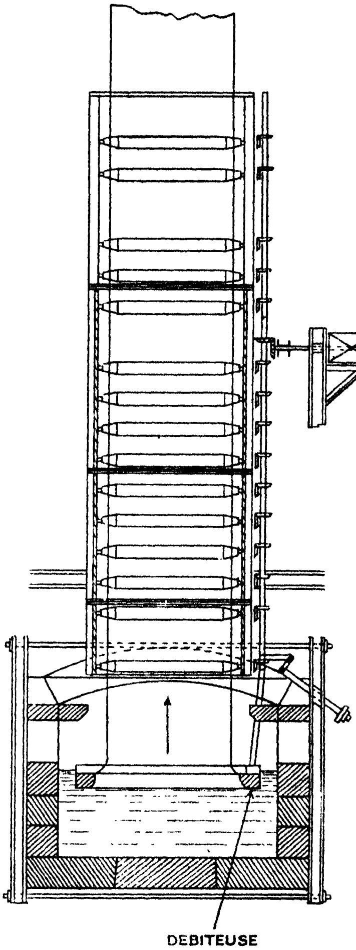


Fig. 38.—Vertical Drawing of Window Glass by Fourcault and Pittsburg Processes.

The Pittsburgh Plate Glass Co.'s process (H. Slingluff, U.S.P. 1556726, 13.10.25) is very similar, but differs principally in that instead of the debiteuse a "drawbar" of refractory material is located a little below glass level to define the line of draw of the sheet. Various coolers of U-form and other shapes are used to chill the edges as they leave the glass surface. The glass composition is similar to Fourcault glass, but the Al_2O_3 is often about 1·5%. Production is approximately 100 ft. per hour for single strength (2 mm.), the width of the sheet being 75 in. though 90 in. and more is drawn nowadays.

(ii) *Horizontal Drawing* is carried out in the Colburn or Libbey-Owens process (U.S.P. 860528, October 12, 1903) put into operation in 1918. In this the sheet is still taken vertically from the glass in the drawing tank but it is then bent over a roller and drawn horizontally. The sheet is gripped by pairs of water-cooled knurled rolls K, Fig. 41, engaging the edges, being driven at 50–25% of the drawing velocity so that a stronger tension exists in the sheet above than below them, and the usual water coolers W are employed on either side of the sheet to control the temperature. The draw is made from glass at about 900° in a forehearth 15 cm. deep divided by a bridge from the main furnace and capable of being heated or cooled from below. Elaborate refractory tiles serve to eliminate draughts above the drawing region. The sheet is bent over a highly polished, air-cooled nichrome roller 15 cm. diameter at R about 63 cm. above glass level after being softened slightly by the burner B. Traction is provided by the two caterpillar belts T faced with asbestos pads and the sheet passed on down a 200 ft. lehr for annealing. Drawing speed varies from 25 to 100 in. per minute for thicknesses of $\frac{5}{16}$–$\frac{1}{24}$ in., a sheet of 1·75 metres being a common width. Each melting furnace supplies one or, at the most, two machines, and as in the case of the other processes very large furnaces are employed in order to obtain glass sufficiently homogeneous by the time it reaches the drawing chambers, a single machine-furnace holding about 400 tons of glass.

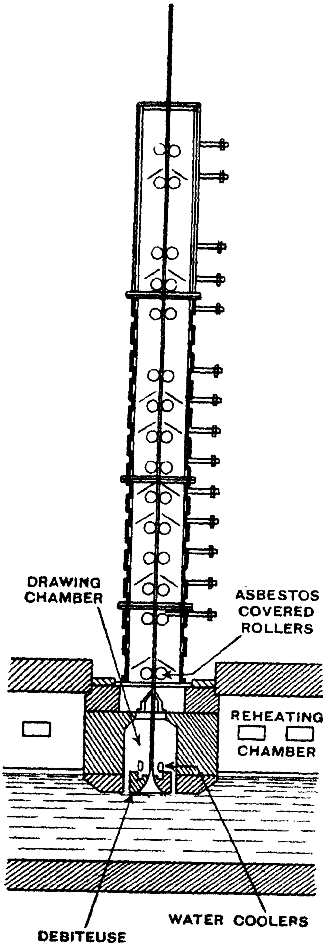


Fig. 39.

(4) **Rolling Processes.**—Lucas de Nehou in 1688 developed a process of casting glass from a crucible or pot on to a metal table and flattening the mass to a sheet by means of a roller. As developed later the process employed mainly oval section pots of 26–36 cu. ft. capacity set in pairs in the arches of each long side of a regenerative furnace. With soda-ash batch 25–40 melts per pot were obtained against only 16–25 with saltcake batch. The batch was charged into the pots in 3 portions of 15, 25 and 2–8 scoop-fulls at intervals of 5 and about 4 hours respectively, each filling being allowed to melt completely before adding another (E. Lutz, Glass Ind. 1930, **11**, 227 *et seq.*). The pots were removed by crane or by hand tongs and carried to the casting table, approximately 394 × 217 in., built up of sections bolted together and there tipped on to its surface. Organic dust was carefully excluded and either sand or glass grains were scattered on the metal surface to prevent chilling of the glass. The use of water-cooled tables and heavy rolls enabled the uniformity of thickness of the sheets to be reduced from 0·620–0·550 in. to 0·395–0·435 in. (to produce 0·25 in. plate when ground and polished). The rolls used had a diameter of 23–26 in. and length of 16·5–18 ft., weighing 20,000–23,000 lb. Ribbing the roll to a depth of 0·03 in. reduced the waviness of the sheet, which was rolled with a velocity of 75 ft. per second by drawing the roll over the casting table by means of wire rope wound round a drum on the roll axle. The rolled sheet was lifted by "stowing tools" having thin fingers to pass between sheet and table and was carried to a lehr ("Stracou") consisting of several chambers through which the sheet was moved step by step on a flat support as it cooled down through the critical range before being sent down a lehr to cool. In spite of improvements this method could not compete with the modern drawing processes and it has been displaced by the Bicheroux and Ford methods (*q.v.*).

Figured Glass.—The original Mason and Conqueror patent (B.P. 13119, 1884) was developed by Chance Bros. and E. F. Chance (B.P. 785, 1890) to make figured glass. A mass of molten glass was cast on to an inclined table leading to a pair of rolls so disposed that with end plates these three formed a trough, and rotation of the rolls fed through a sheet of glass which then went through a second set of rolls embossed to impress the desired pattern on the still plastic sheet.

The Bicheroux Process in its later form (G.P. 334699, 16.11.18) followed the Chance method of casting into the space between rolls and table, and using a moving carriage to catch the sheet produced, tilting the table as the glass was put through the rolls. The sheet was caught on a series of flat topped cars which were drawn along at the speed of rolling to receive the sheet. As soon as the rear edge of the front car came opposite a guillotine a narrow strip of glass was sheared out between it and the car following, after which the front car was hurried away by cable haulage to the lehr front where stowing tools lifted the sheet into the lehr, which in this method is up to 700 ft. long. The success of the method depends in large measure on the principle of pouring the pot by turning on an axis passing through the lip at the pouring point (Fig. 42*b*) and not through the centre of the pot as in the older casting process (Fig. 42*a*). The velocity of rolling is 2 ft. per second or more, the sheet size 11 ft. wide × 100 ft. long for 4 mm. thick or 45 ft. long for 8·5 mm. By this modification of the older process it is possible to stack 100 sheets of $\frac{11}{32}$ in. glass in the space formerly necessary for 14 sheets of $\frac{15}{32}$ in. and sheets about $\frac{1}{8}$ in. thick can be rolled.

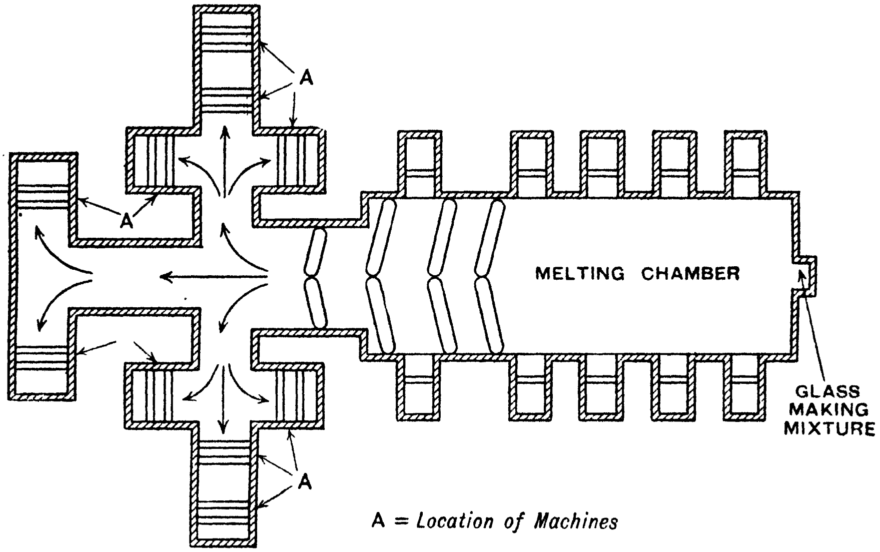


FIG. 40.

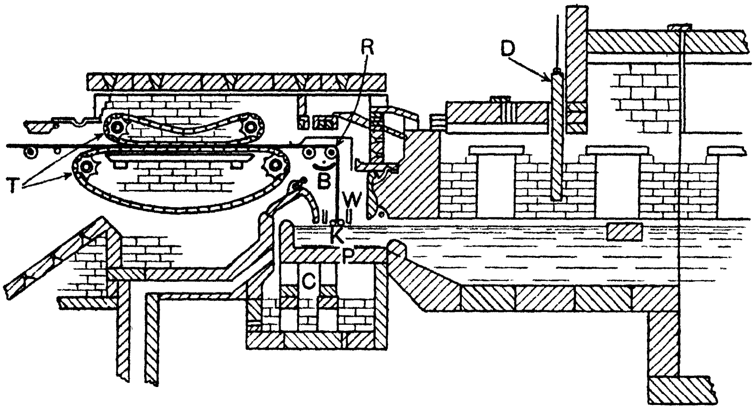


FIG. 41.—HORIZONTAL DRAWING OF WINDOW GLASS BY COLBURN AND LIBBEY-OWENS PROCESS.

The Ford Process is a continuous one in which glass flows from a furnace 36 ft. long × 20 ft. wide × 5 ft. deep, Fig. 43, down a 14 in. wide spout controlled by gates to the pass between water-cooled rollers of 9 in. and 48 in. diameter, the lower one driven at about 40 in. surface speed per minute. A sheet 40 in. wide suitable for motor-car screens is produced as a ribbon which passes straight into the lehr 440 ft. long. In the first section the temperature is 593°C., dropping by 28° per section to 343°, after which the sheet cools to room temperature before emerging. The time to traverse the lehr is 2 hours 20 minutes. The unit has a capacity of 16,000 sq. ft. per day. In Britain the process has been developed by Pilkington Bros., Ltd., to make very much wider sheets.

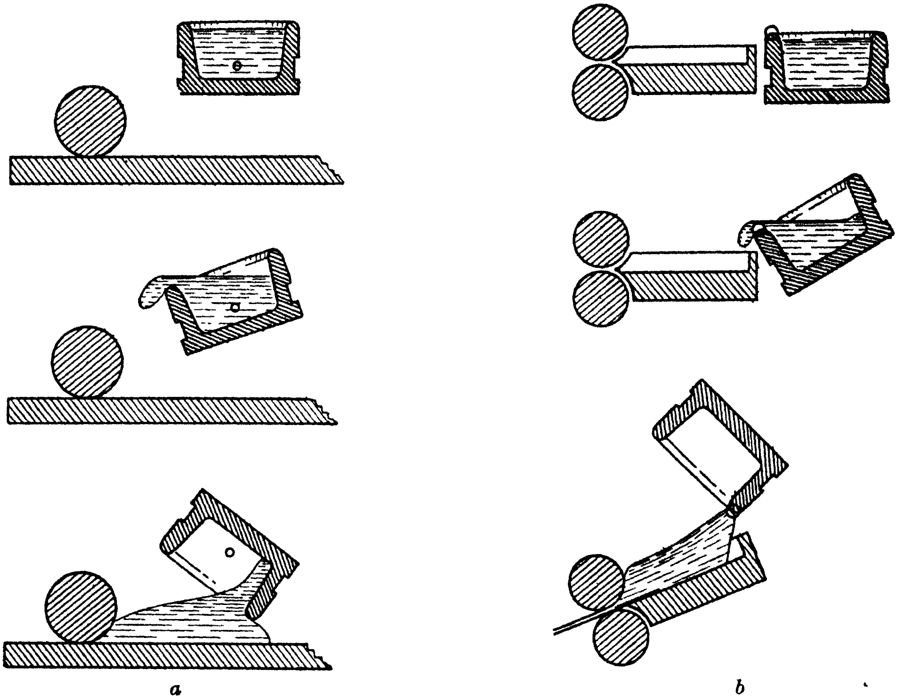


Fig. 42.

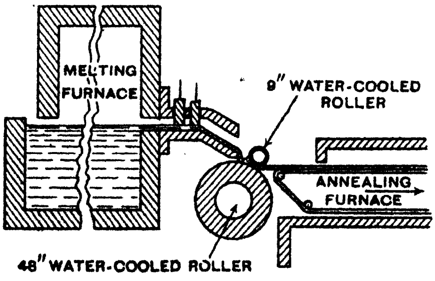


Fig. 43.

Drawing Processes.—*Glass Threads and Wool.*—This is made by three types of process: (*a*) Drawing by revolving drums either from rods softened by blowpipe flames or from drawplates provided with a number of orifices located in the bottom or sides of a small furnace melting cullet or glass previously prepared in the form of marbles to facilitate constant feeding in of material. Threads of mean diameter 0·02–0·03 mm. are commonly produced. Several fibres may be spun on to one drum to form a thick layer which is then cut longitudinally to form a mattress or blanket for insulating purposes when opened out and stitched or sprayed with adhesive. (*b*) Dropping thin streams of molten glass on to a disc revolving at high speed so that threads are thrown off by centrifugal force. (*c*) Entraining thin streams of molten glass by high pressure jets of steam or air so that the mass is attenuated to fibre dimensions (U.S.P. 2133235, 2133236, 2133238). The last-named process gives the finest fibres (0·01 mm.) and is used by the Owens-Corning Fiberglas Corporation of U.S.A. The product has been made into yarn by combing and spinning and woven by ordinary textile processes to produce cloth and tape that has many uses in the chemical, fire preventing and electrical and heat insulating industries. Production is stated by L. von Reis to be, in kg. per hour, 0·5–1·0 for the rod, 1·0–1·5 for the orifice, 10–60 for the centrifugal and 100–500 for the blast process.

"*Thermolux Glass*" (P. Modigliani, U.S.P. 2011252 and 2081060) is made from threads spun on to a drum from two directions to form a criss-cross matt a few threads thick. This is then cut, opened out and laid between two sheets of glass which are sealed round the edges to hold them in register leaving the threads held by friction only. The composite sheet has such excellent light diffusing qualities that although 25–50% of the incident light is absorbed, that passing through gives better illumination in a room than clear glass. The heat-and-sound insulating properties are also good. The heat transmissions in B.Th.U. per sq. ft. per °F. for clear glass $\frac{1}{12}$ and $\frac{1}{4}$ in. thick, double $\frac{1}{12}$ in. with 6 in. space between, Thermolux with $\frac{1}{8}$ in. glass fibre interlayer and double Thermolux with 6 in. space, are respectively 1·16, 1·10, 0·58, 0·74 and 0·38.

Glass Building Bricks or Blocks.—By pressing in two halves and then uniting, hollow glass building blocks can be made. The assembling is either done hot immediately after pressing by superposition in a jig followed by further pressure to weld, or the halves may be annealed, taken from the lehr at approximately 430° and suspended by suction or other means with their edges in a bath of molten aluminium, aluminium-silicon alloy or other binding medium, after which they are placed together in correct relation, clamped and the excess metal on the joint removed by a hot soldering iron (W. P. Zimmerman, M. K. Holmes and Owens-Illinois Glass Co., U.S.P. 2149246, 28.2.39). In other methods the two halves are rotated, while clamped together, below a thin stream of glass falling from a feeder on to the joint. By assembling whilst the halves are hot a partial vacuum is created inside, improving the insulating properties of the blocks. Walls may be built of them, but they are not intended to carry load beyond their own weight, and metal reinforcing strips are usually built-in every few feet of height. It is possible to produce good light-dispersing qualities by pressing fluted patterns and assembling with the flutes of one half at right angles to those of the other half of the block. Coloured or patterned sheet or fibre mats may be inserted before assembly, and aluminium may be sprayed on to reduce the light transmission but also decrease markedly (by 40%) the thermal loss by radiation (B. Long, J. Soc. Glass Tech. 1937, **21**, 430). E. Booth (Nature, 1937, **139**, 977) found the thermal transmission, excluding radiation, for ordinary 16·5 × 16·5 × 10 cm. hollow glass blocks was 0·39 g.-cal. per hour per sq. cm. per °C. difference between the 16·5 × 16·5 cm. faces.

ANNEALING OF GLASS-STRAIN.

The free cooling of plastic glass results in the solidification of the outer layers whilst the interior is soft so that further cooling causes compression on the surface and tension within. In glassware this state of strain is removed to a very large extent by the process of annealing in order to give stability to mechanical and thermal shock. The residual stress permissible varies with the function of the glass article. It is measured by the birefringence it produces (for most glasses a stress of 1 kg. per sq. cm. gives a birefringence of about 3 mμ per cm) and for optical glass a birefringence of only 5 mμ. per cm. path may be tolerated whilst 50 mμ. has been proposed as an upper limit for plate glass by L. H. Adams and E. D. Williamson (J. Franklin, Inst. 1920, 190, 597, 835), and about 100 mμ for general commercial glass. A strain of 60 mμ. per cm. corresponds to a stress of

$$(60 \times 10^{-6}) \div (3 \times 10^{-7})$$

or 200 kg. per sq. cm. Even if the glassware is held at a temperature below that at which it deforms until all strain is relieved it cannot cool freely without setting up a temperature gradient from inside to outside, and when this gradient disappears at the final low temperature, permanent stress will be left as compression on the surface and tension inside. By slow cooling through the temperature range within which relief of stress is possible so that the temperature gradient across the glass in passing through this range is small, it is possible to prevent very largely this development of stress and strain on reaching room temperature. The important temperatures are M_g corresponding with the maximum on the thermal expansion curve (*see* Fig. 4) (sometimes called the softening point or upper annealing temperature) and T_g, the transformation point at which a break occurs in the temperature–property relationships. This interval is known as the *annealing range* and is that during which sudden cooling will reintroduce strain into an article that is strain free. For safety the slow cooling within the annealing range is continued in commercial annealing processes well below T_g, usually at least 50°C. below. This cooling rate is about 1½–3°C. per minute. At M_g the relief of strain is a matter of minutes, at T_g of hours. The time as well as the temperature effect should not be overlooked. Adams and Williamson defined their annealing temperature as that at which the strain falls from 50 to 2·5 mμ. per cm. path in 2 minutes.

The annealing temperatures may be taken from the expansion curves, or may be optically determined from observations of the temperature at which a rod of strained glass gives a black field when viewed between crossed Nicol prisms. Values found by A. Q. Tool and J. Valasek (J. Bur. Standards Sci. Papers 1920, **358**) are quoted below.

Type.	Lower annealing temperature.		Upper annealing temperature.	
	Expansion Method.	Optical Method.	Expansion Method.	Optical Method.
Dense flint . .	460°	—	490°	—
Medium flint .	455°	460°	485°	510°
Light flint . .	485°	485°	525°	510°
Barium flint .	520°	515°	560°	550°
Light crown .	495°	480°	525°	530°
Borosilicate crown . .	515°	525°	565°	550°
Light barium crown . .	575°	570°	605°	610°
Dense barium crown . .	575°	605°	630°	625°

Soda–lime–silica glasses anneal in the range 540–610°, and resistant chemical-ware glass may need as high as 630°.

The effect of various oxides on the annealing temperature was studied by Turner and co-workers and by G. Gehlhoff and M. Thomas (Z. tech. Physik, 1925, 6, 333). Oxides of Na, K and Pb progressively reduce it when substituted in the parent glass $\mathrm{SiO_2}$ 82, $\mathrm{Na_2O}$ ($\mathrm{K_2O}$) 18%, to replace $\mathrm{SiO_2}$; CaO, MgO and ZnO and $\mathrm{Al_2O_3}$ increase it; BaO and $\mathrm{Fe_2O_3}$ have little effect at first and in large amount reduce it; whilst $\mathrm{B_2O_3}$ increases it up to about 20% $\mathrm{B_2O_3}$, after which further additions cause a decrease.

Strain is detected in glassware by inspection in polarised light. Modern instruments give a large though slightly non-uniform field but permit easy manipulation of the ware inspected. The incident light is nearly always polarised by reflection from a black glass plate and in one type the second polarisation is similarly carried out, though usually a Nicol prism eyepiece is used for this purpose. Recently the material "*Polaroid*" has been used to replace the Nicol. To render the birefringence effect more easily visible a sensitive tint plate (mica or selenite) is employed.

Lehrs.—The actual annealing process is carried out either in a kiln (now only used for very heavy articles such as blocks of optical glass or pavement lights) or a lehr. In the first of these the ware is stacked in trays packed with sand and insulating material and the whole is heated up and then cooled slowly. Lehrs are now usually of muffle type though a number of open-fired ones exist. They consist of a tunnel 60–75 ft. long and 3–8 ft. wide for ordinary work (but may be 300 ft. long or more for window glass) down which runs on a track a string of iron pans, or a continuous belt. Modern practice favours a wire mesh belt because of its small heat capacity, since it returns outside the lehr and must be heated up again. Belt speeds run between 20 and 70 ft. per hour and can be varied to suit the ware. The fuel consumption has been much reduced by careful insulation of the refractory lining of the first part of the tunnel where the ware is kept hot enough to relieve strain, thereafter the temperature is allowed to fall along the lehr at a rate that does not cause reintroduction of strain to any serious extent. If the input is sufficient the ware may take in enough heat to anneal itself without any external supply, but usually either gas, oil or electrical heating is provided. Electric lehrs have the advantage of excellent control and low maintenance costs. The insulation is reduced down the lehr in steps and at the cool end air is drawn in by a fan. Similarly hot gases can also be drawn in from the inlet end to keep up the temperature further down the lehr. A refinement, not yet general practice, is the use of a separate narrow lehr to take the production from each individual machine so that the annealing schedule may exactly suit the article made. Fig. 44 shows diagrammatically a modern type of lehr.

Hardening of Glass.

This may be carried out either by the process of De la Bastie or by that of Siemens. In the former, discovered in 1873, the glass article, while still red hot, is quenched in a bath of oil or fat, the actual temperature of both glass and the bath, that is, the quenching range, depending both on the composition and thickness of the glass. Sodium–calcium glasses can withstand a greater quenching range than the lead glasses. The process results in the sudden chilling of the outer before the inner layers, so that the surface layers undergo greater shrinkage, causing them to be subjected to compression, whilst the inner layers, on the other hand, are in tension. Glass in this condition becomes less brittle, is more elastic, and capable of withstanding mechanical shock and sudden change of temperature, but if the surface is once broken the whole mass shatters.

In Siemens' process, the temperature of pressed glass articles is rapidly but uniformly reduced in special moulds, or between metallic or clay plates maintained at a suitable temperature. Pavement lights treated in this manner resist cutting by a diamond. (*See* "Toughened Glass," p. 608.)

Compound Glass, the basis of the "*Durax*" water-gauge tubes, was developed by Schott to give the same resistance to shock and change of temperature as hardened glass. A gathering of glass 16^{III} is made over 59^{III} and the cylinder drawn into tubing. The former has the larger thermal expansion (and contraction), so that on cooling the outer layer is under compression and the inner under tension. When the tubing is heated up both compression and tension become relaxed. Glass 59^{III} which forms the inner layer is also very resistant to the action of water and steam.

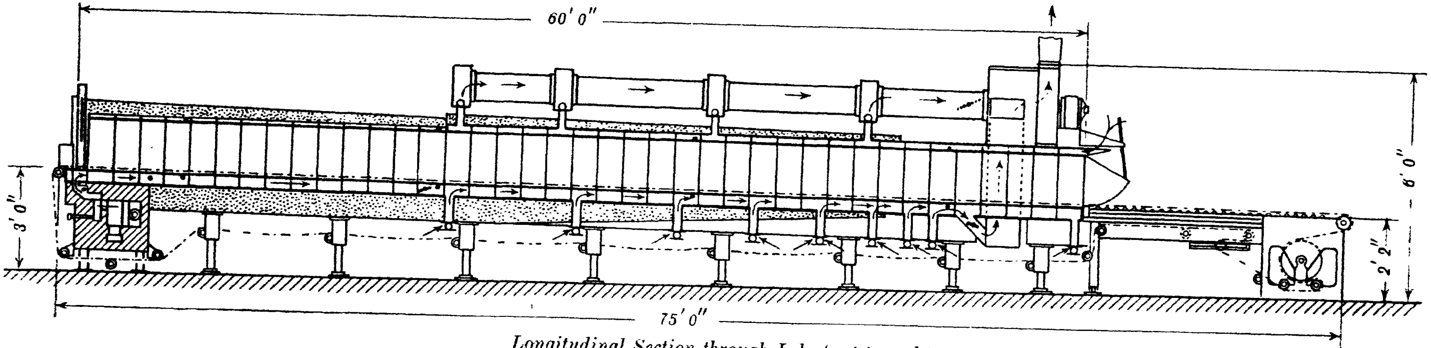
Cold Working of Glass.

Processes applied to glass after fabrication in the plastic condition and subsequent annealing are grinding and polishing, cutting and engraving, etching, painting or other form of decoration such as silvering.

Grinding and Polishing is carried out on plate glass after rolling by the following methods:

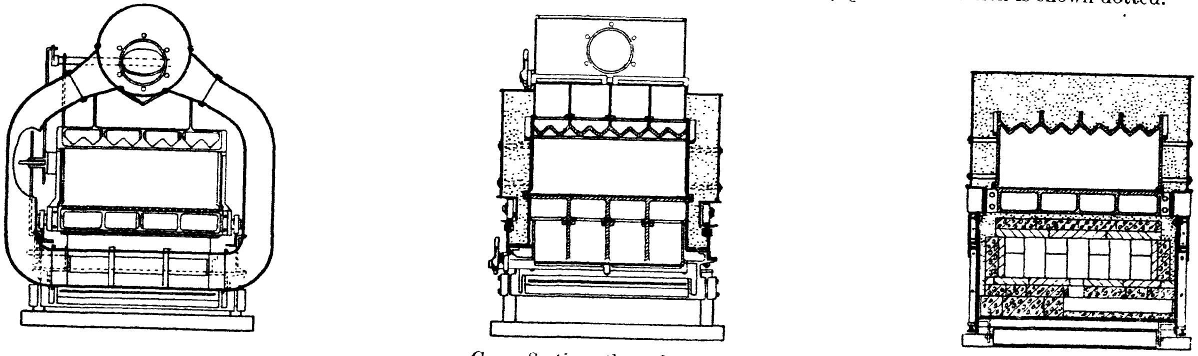
Discontinuous.—In the old method circular tables 24–36 ft. in diameter weighing 75–80 tons were mounted on rails to move between the grinding and polishing stations and at each end were registered over, and fastened to, driving shafts which revolved them from below (Fig. 45). Their speed was 20–28 r.p.m. taking up to 500 h.p. for grinding, and 13–22 r.p.m. taking up to 700 h.p. for polishing, whilst tools charged with abrasive or polishing material (rouge) rotated eccentrically in contact with the glass. The grinding with sand and three grades of emery took 1–1¾ hours per side and the polishing 1–1½ hours.

Semi-Continuous.—The circular table was awkward to fill economically with rectangular fragments, and with the introduction of the more rapid methods of raw plate production a straight line track system of grinding and polishing was followed, in which the sheets were laid upon cloth on flat cars and were bedded with plaster to fill the joints. The cars are then sent down



Longitudinal Section through Lehr (not to scale).

The arrows represent the flow of the heating and cooling media in their respective flues whilst in the bottom flue may be seen the valves which can be adjusted independently to allow the admission of the amount of cooling air needed. The scientifically graded insulation is shown dotted.



Cross Sections through Lehr.

On the left is a section through the vertical flues. Check dampers are provided in top and bottom flues enabling the draught in each flue to be controlled independently. The central figure shows a section through a cooling valve in the top flue and a dilution valve in the bottom flue. On the right is a section through the combustion chamber. The hot gases pass through the vertical flues into four separate compartments extending longitudinally which together comprise the heating flue.

FIG. 44.

(By permission of British Hartford-Fairmont Syndicate.)

the very carefully levelled track below a series of grinding heads (43 at Ford River Rouge Works) and polishing heads (36 at River Rouge), sufficient space being provided for thorough washing to remove each grade of abrasive (sand, garnet, carborundum, etc.) before passing to the next and for inspection before polishing. The pressure on the grinding heads is 12–40 kg./cm.^{2} and on the polishing from 4 kg./cm.^{2} at the start to 2 at the finish of the operation, and the the speed of travel of the cars about 3 ft. per minute. Various washing processes have been evolved to overcome the caking of the rouge on the polishers in these continuous processes. When one side of the glass has been polished the sheet is turned over and the process repeated. In some methods the cars go to a second line of grinding and polishing heads, but in the Pilkington method they are returned to the starting point below the track which is built at a higher level for the purpose.

Fully Continuous. — The most up-to-date method of dealing with the continuous ribbon from processes such as that of Ford is to grind both top and bottom surfaces simultaneously. Pilkington Bros. and J. H. Griffin (B.P. 469951, 5.2.36, *also* B.P. 492288, 17.3.37), do this by adjusting the lower set of tools to precise alignment and providing pairs of rollers to support the sheet between the pairs of tools and at the same time feed it forward. The rubber covering of the rollers is adjusted to give the necessary resilience, the upper one being softer than the other (B.P. 491851, 1937), and means are provided (B.P. 489661, 1.2.37) for playing on streams of water to wash grains of sand away from the rollers to avoid crushing the glass.

Other Grinding Processes.—*Lens Grinding.*—A number of glass blanks are secured to a block of cast iron which is turned to the appropriate curvature and is coated with a mixture containing boiled wood-pitch and resin. After cooling the block is screwed on to a vertical spindle which is caused to revolve whilst a "tool" of cast iron of opposite curvature to that of the block is moved over the surface under pressure, being oscillated over that surface by an arm resting on its centre, the tool being free to revolve by the friction with the block below. Emery or carborundum mixed with water to a thin cream is supplied to the work and at intervals is washed off thoroughly and replaced by a finer grade of abrasive. At each stage all marks from the previous process must be removed before proceeding to the next. Finally rouge is substituted for the abrasive and the tool is changed for one covered either with felt, if a rough figure is permissible (common lenses and some spectacles), or with pitch if the highest optical perfection is required (photographic and other optical parts). A number of spindles are commonly driven from one shaft, friction clutches being provided to each spindle. The greater the lens curvature the fewer the pieces that can be dealt with on one block.

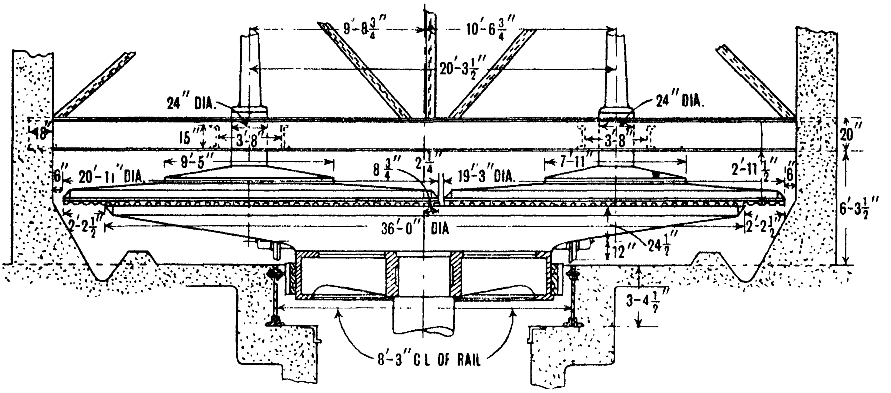


FIG. 45.—GRINDING PLATE GLASS. DISCONTINUOUS PROCESS.

Stopper and Tap Grinding.—The stopper blanks (pressed as a series of radiating "spokes" from a centre cup and then broken off, or for larger ones individually made) are knocked into wooden chucks on horizontal spindles and a piece of springy sheet iron bent up on a mandrel to the desired taper is passed over the part to be ground and fed with abrasive and water, being pinched together by pressure applied to the ends which are bent out to form wings. On a similar spindle running parallel with this is an iron plug of the same taper which is used to grind the bottle mouth (or barrel of the tap), after which the stopper and bottle or plug and tap are ground together.

Mouth Grinding, e.g. of tumblers, is carried out by holding the tumblers upside down in a cup on a stone revolving on a vertical axis. A small tube passing through the axis of the stone supplies water and the glass is rotated about the axis of the cup which is slightly eccentric to that of the stone. Alternatively the tumblers may be put in holders right way up and brought up to stones driven at 1,700 r.p.m. by individual motors (*see* E. Venis, J. Soc. Glass Tech. 1937, **21**, 310) in a revolving machine carrying 6, 8 or 12 heads, Fig. 46. Various types of stone are used, 150 P.25 "*Aloxite*" being typical. The latter type of machine keeps the drive mechanism above the water.

Bottom and Decorative Grinding is carried out by machines carrying one or more stones revolving about a horizontal axis and provided with holders for the work which can be brought up to the stone by pedal as for bottom grinding, or which are held up to the stone by counterweights and at intervals are held away whilst the holder is indexed round a fraction of a turn before being brought up to the stone again, as is done in grinding flutes and " olives " on the sides of tumblers and the like.

THE DECORATION AND AFTER TREATMENT OF GLASS.

These processes may be divided into two classes, namely: (1) those carried out at the furnace during the formation of the article; (2) those dependent on the treatment of the surface. To the former belong such processes as casing, spinning, filigree and mosaic working. The second class is divisible into two groups, according as the surface is treated by mechanical means, such as those involved in decoration by grinding, cutting, bevelling, polishing, engraving, sand-blasting and frosting; or by the action of chemical reagents, such as in etching, silvering, iridising and in glass painting. In rather a different category is the art of treating glass tubing or rod by lampworking or bench glass-blowing.

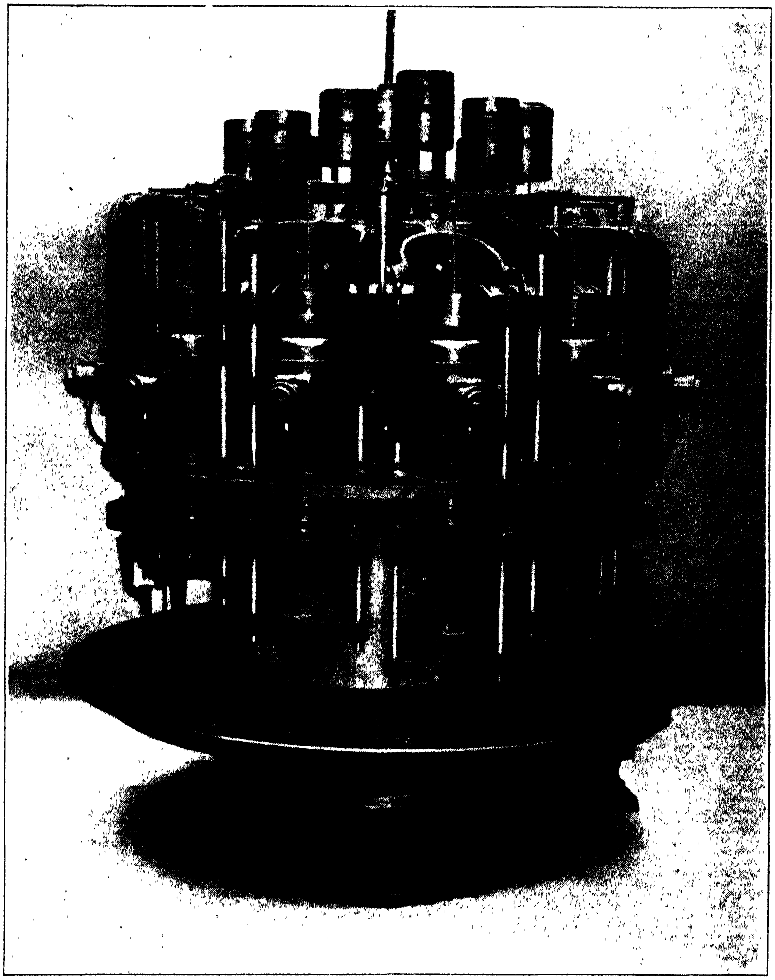


FIG. 46.

Casing consists usually in spreading a uniform, thin layer of colour over an article of colourless glass. The coloured glasses most commonly used are ruby, blue and opal. The essential conditions for casing are that the glasses shall have approximately equal coefficients of expansion and similar temperature-viscosity characteristics and be soft or plastic. Glasses of fairly high lead content are very suitable for such treatment. One method of carrying out the operation is to make a gathering of the colourless glass, to blow it up slightly, and then dip into a pot of the coloured glass in such a way that a uniform outer layer is obtained. The combined gathering is then worked up by turning or blowing in the usual manner.

Banded glass, feather glass, filigree glass and the insertion of an enamel backing in thermometer and other tubing are all special examples of casing. The enamel backing of tubing is a simple example. One method of making it consists in preparing a rod of opal glass and inserting a length of it in a vertical recess in a mould. The parison of colourless glass is introduced into the mould so as to come into contact with, and pick up the opal rod, after which the parison is marvered further to complete the union. A further gathering of colourless glass to cover the opal is then made and the whole mass drawn into tubing in the ordinary way.

For details of manipulative methods of decorating glassware at the furnace the reader should consult R. Hohlbaum, "Zeitgemässe Herstellung, Bearbeitung, und Verzierung des feineren Hohlglases," Wien und Leipzig, Holder, 1910; Apsley Pellatt, "Curiosities of Glass-making," London, D. Bogue, 1849, contains a good account, but is unfortunately long out of print.

Decorative Processes Applied after Fabrication.—*Cutting.*—The design is outlined in waterproof chalk or paint and is then roughed out with coarse abrasive. This was once done on an iron wheel revolving on a horizontal axis fed with sand and water, but most work is now done on synthetic abrasive stones, *e.g.* "*carborundum*" of No. 80 or 120 grit (*see* Fig. 21). The smoothing cut is then made, and here the Craigleith stone once employed has given place to a fine grade of "*Alorite*" or similar abrasive of about 150–180 grit. The speed of rotation varies with the type of work and size of stone. In the older installations surface speeds of from 600 to 1,700 ft. per minute are used. The polishing which was once done on wooden wheels with pumice powder followed by tin oxide ("putty") is nowadays carried out in a bath composed, for full lead crystal glass, of approximately 2 parts by weight strong hydrofluoric acid, 2 parts strong sulphuric acid and 1 part water, worked at 40°C. The acid polishing of glasses of other types is not so easy and calls for different bath compositions.

Intaglio Work is similar to the above in that abrasive stones are used, but finer and smaller stones are employed, the work is held below instead of above the spindle, and the design may be left matt or may be polished as best accords with the decoration applied.

Engraving again is similar but still more delicate. A very light spindle is used with a taper bore chuck to take any one of numerous spindles provided at the opposite end with a copper disc. The range of size of disc is from 2 to 3 in. down to pin head diameter, and from about $\frac{1}{4}$ in to $\frac{1}{32}$ in. in thickness. These are charged with a mixture of abrasive and oil, and are used with rare skill to produce designs on the ware much as an artist would draw on paper.

Sculpture—Use of Hand Tools.—In recent years much use has been made of a small hand motor, notably the Bosch machine, which takes small abrasive tools enabling work of an engraving or intaglio type to be carried out on large panels of glass which could never be dealt with by the older methods. More robust motors with flexible drive to a hand piece carrying the grinding wheel are used for broader and deeper effects. The artist works on the vertical glass panel using a stream of water to cool the glass and carry away the debris.

Bevelling, e.g. of mirrors, may be carried out by hand on the flat face of grindstones rotated about a vertical axis or on abrasive rollers turning on a horizontal one. Most work is now done by automatic machine in which the sheet is clamped in a frame that can be traversed past two rotating abrasive wheels at the desired (adjustable) angle, the first to make the rough and the second the smooth cut. Suitable stones are "*Crystolon*" 80-H vitrified for the first and "*Alundum*" 220-K vitrified for the second process, though sometimes only one medium stone is used. Felt and rouge give the final polish. For rounding the edges of automobile screens "*Alundum*" 150-N vitrified bond wheels are used.

Slitting or Cutting off of sections of tube is done with very thin wheels with a flexible, *e.g.* rubber bonded, wheel composed of 120-R "*Crystolon.*" These are used with water at a comparatively low speed.

Etching is accomplished by hydrofluoric acid of various strengths and with other agents added, or by fluorides in the presence of other acids. For matt effects silicofluorides are necessary, forming protecting crystals over part of the glass so that material is removed to different depths to give the irregular light-scattering effect (L. Honigmann, Glastech. Ber. 1932, **10,** 154). Lead glasses etch most easily, lime glasses are more resistant, and borosilicate glasses of the chemical ware and pyrex types are very difficult, if not impossible, to etch satisfactorily. Of the acid fluorides commonly used for the purpose that of ammonium gives the coarsest and potassium the finest etch structure, so that acid solutions of potassium fluoride are commonly employed for giving a satin matt finish to cosmetic and pharmaceutical bottles, *e.g.* KF 10, HCl 1, water 100, used at about 50°C., whilst etching pastes for badging glassware commonly comprise a saturated solution of $(NH_4)HF_2$ in H_2SO_4 with loading material to give the required consistency. Blanc fixe is much used together with gum, glycerin, zinc chloride, sodium silicate or flour paste for this purpose. The internal frosting of electric lamp bulbs is an example of control making possible reproduction of conditions. Here the etching solutions are two, a quick rough etch followed by a fortifying one (M. Pipkin, Ind. Eng. Chem. 1926, **18,** 774; B.P. 228907, 4.2.25; 254316, 23.6.26), which rounds off the sharp crevices left by the first and so restores much of the strength of the bulb. The quick etch is pumped in the form of a slurry (composition 42 $(NH_4)HF_2$, 20 $BaSO_4$, 3·5 $NaHSO_4$, 27·5 HF, 7 dextrin, +water q.s. to give 18–25% HF in the mixture) up a number of nozzles over which a tray or frame full of bulbs is inverted. After spraying for a few seconds the flow is stopped and the frame is lifted off and moved down to a further set of nozzles where the bulbs are sprayed with a diluted mixture containing only about 7·5% HF. In some processes a brief water spray is used to produce this by diluting the first mixture remaining on the walls. The next set of nozzles spray with rinsing water and then the bulbs are dried by jets of warm air.

For line etching, dilute acid, *e.g.* HF 1, water 4–10, with or without H_2SO_4 1, is used at a temperature not above 30°.

The decorative capabilities of etching are increased by the application of resists to the glass to protect those portions which are to be left unacted upon. These may be of beeswax and tallow, with or without paraffin wax as used for needle etching, a process employing a mechanical device to move a needle or needles to cut patterns in the wax through which the etching fluid can act. Or the resist may consist of (*a*) asphalt 5, resin 2, tallow 1, Venice turpentine 2, turpentine 12; (*b*) asphalt 5, resin 3, beeswax 1·5, Venice turpentine 1, turpentine 8, and be used to form transfers which are applied to the glass on suitable paper so that the etching paste painted over with a hair mop may form a badge or design. The wax resists lend themselves to mass production coating by immersion, whilst the second type are best for transfer work. Tinfoil is used as a resist in marking some graduated apparatus, the design being cut *in situ* with a sharp knife.

Ice Flower Patterns are produced by applying strong bone glue to a sandblasted surface and drying under controlled conditions. When dry, the sheet of glass is placed in a warm room or hot cupboard, and the contraction of the glue flakes off pieces of glass. The size of these depends on the thickness and strength of the glue coating and the drying conditions. The fragments may be collected, remelted with a little preservative, and after straining free from glass splinters used again (Cailletet, Comp. rend. 1902, **134**, 400).

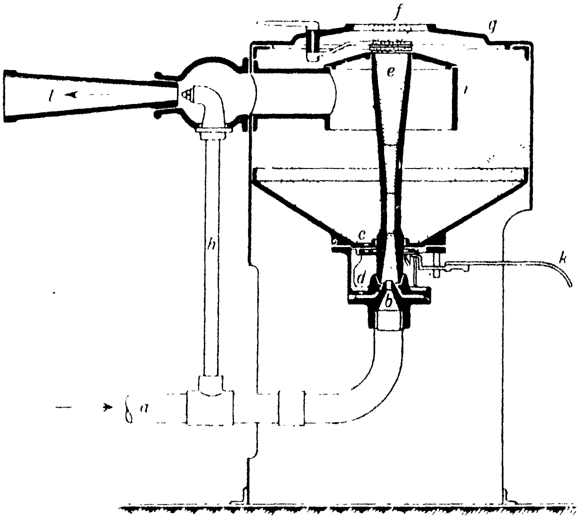


FIG. 47.

Alternatively a quicker and less durable method which does not destroy the glass surface is to coat with a varnish of gum sandarac 18, gum mastic 4, in the mixed solvent benzene 40, ether 200, applied to a perfectly clean surface. Another method is the application of so-called crystallising varnishes using a cellulose ester base.

Sandblasting, first applied in 1870 by B. Tilghman in America, is carried out by directing against the glass a jet of grains of sand entrained by a compressed air or steam-blast, the former being more usual. It may be applied in an enclosed cabinet provided with strong draught to prevent silica dust reaching the operator through the holes provided for introducing the work. The sandblast is pedal controlled, and issues from a nozzle in the bottom of the upper part of the apparatus to play on the work which is turned in all directions as required by the operator. Used sand collects in the bottom of this chamber (Fig. 47) and drains back to the base whence it is used over again if compressed air is employed. In this case all water must be filtered out of the air supply line to prevent caking of the sand. Continuous apparatus for sandblasting sheet glass exists in which the sheets pass over a table across which runs a channel containing the sandblast jets. The glass itself forms the seal to this by resting on resilient material lining either edge. Other work too large for treating in a cabinet is handled in a dust-tight room in which the operator moves, in special clothing with a head piece like a diver's helmet, and carries a flexible hose with valve-controlled jet to apply the sandblast. Apart from its use in obscuring large sheets of glass, the main application is in decoration or badging by means of stencils made of metal, rubber or thin paper coated with strong glue containing some non-drying agent to preserve a rubbery consistency. The last of these is applied to the glass and the design cut through so that it is only used once, whilst the first two types are suited to repetition work. Much use in recent years had been made of the sandblast in producing sculptured effects on architectural panels. The glass is protected by stencils and sandblasted once. Parts are then covered over and further sandblasting is done on the remainder to give a deeper relief and the process repeated to produce the desired effect. Treatment of sandblasted surfaces with etching mixtures produces a matt effect which cannot easily be obtained by either treatment alone.

Edge Melting and Cracking Off Machines.—The production of tumblers and lamp bulbs by press and blow machines (*e.g.* Miller) or paste mould machine (*e.g.* Westlake or Corning), and of illuminating bowls and many other articles, necessitates the removal of part of the blank called the "cap" next the blowhead and sometimes also of the opposite end (*e.g.* open-ended cylinders).

Cracking Off consists in making a scratch with a diamond or similar tool by moving the blank on a flat table against the tool held at the correct height and then transferring the work to a rotating table where a number of pin point flames (Bornkessel burner) are brought to a focus on the glass surface at the height of the scratch (Fig. 48). A few seconds is enough to cause the crack to spread completely round effecting a clean cut off. The surface is then ground true as already mentioned and is subsequently fire-polished (*vide infra*). Both thick and thin walled articles can be so treated, but cheap mass-produced thin walled articles are generally now made from blanks by the process next described.

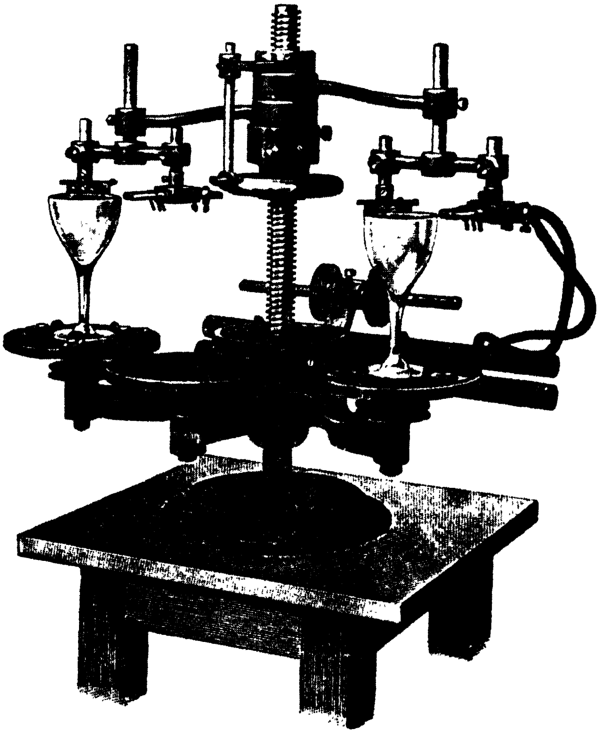


FIG. 48.—CRACKING OFF MACHINE.

Melting Off is done by holding the articles, more specifically tumbler or lamp bulb blanks, in a suction cup or other holder which is rotated whilst sharp, very hot flames (oxygen is sometimes used to supplement the air supply) play from ring burners surrounding the glass at the melting off line. By balancing the pressure of the flame and the speed of rotation, it is possible to melt off the cap which falls to waste down a chute, leaving a beaded edge on the article which is neither turned inwards nor outwards and is not of an objectionable size.

Fire Polishing is applied to the edges of articles that have been smoothed by grinding, *e.g.* tumblers. Fig. 49 shows a Knight fire finishing machine in which the ware is stood on rotating tables on a travelling belt which takes them down a narrow tunnel heated at the top by flames which increase in intensity down the tunnel to give a gradual heating which prevents shattering when the hot polishing flame is applied locally at the edges of the ware. Asbestos discs are often dropped inside to shield the bottoms of thick ware.

The process is also applied to pressed glassware to remove the marks left by the moulds on the glass surface. This is effected by holding the glass on a punty in a small hot gas- or oil-fired furnace called a "glory hole," the aim being to produce an intense heat to glaze the surface without causing deformation of the main body of glass.

Deposition of Reflecting Films on Glass.

(1) **Silvering.**—Drayton in 1843 introduced silvering to replace tin amalgam for mirrors, and Liebig in 1867 made the process a commercial success. The two classical processes are the Rochelle Salt and the Brashear.

The Rochelle Salt Process ("*Hot Process*").—Solutions required are (*a*) reducing solution: $AgNO_3$ 2 g., Rochelle Salt 1·7 g., water 1,000 ml.; (*b*) silver solution: A. $AgNO_3$ 10 g., water 100 ml.; B. $AgNO_3$ 3 g., water 30 ml. To solution A add concentrated NH_4OH until the precipitate first formed is dissolved, after which solution B is added drop by drop with shaking until a slight permanent darkening of the solution indicates the formation of silver oxide. Dilute to 1,000 ml. and filter. In use mix equal volumes of reducing and silver solutions and immerse the chemically clean glass surface at 20–30°C. The quantities specified will coat 400 sq. cm. thickly.

The Brashear Process ("*Cold Process*") gives a brighter reflecting surface and is much used for instrument work. Solutions required are: (*a*) reducing solution, cane sugar 90 g., nitric acid (sp.gr. 1·42) 4 ml., water 1,000 ml., boiled 5 minutes and allowed to cool; (*b*) A. silver solution, $AgNO_3$ 20 g., KOH (pure stick) 10 g., water 400 ml.; B. $AgNO_3$ 2 g., water 30 ml. The precipitate produced by the KOH in solution A is dissolved by addition of ammonia as in the Rochelle salt process, and solution B is used as there described. For use take 1 vol. reducer to 4 of silver solution. The silver solution specified above will cover 800 sq. cm.

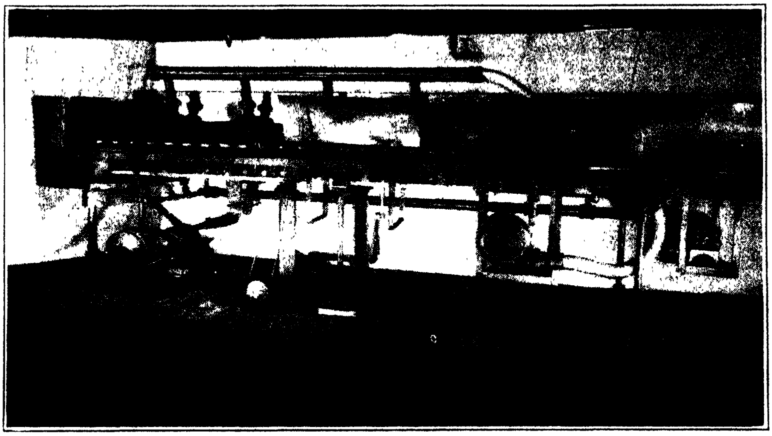


FIG. 49.

The danger of explosions from silver amide formation is minimised by storing only *dilute* solutions of silver and by keeping all vessels clean so that the formation of dried up deposits is prevented. Serious trouble has resulted from failure to observe these precautions. However deposited, silver films are usually strengthened and protected by electrolytic deposition of copper from a bath of low acidity. After washing and drying the film is backed by a shellac varnish free from impurities liable to damage the film (*e.g.* acid, sulphur, chloride) and an asphalt lacquer is frequently applied over this. For some purposes lead is electro-deposited on the copper to build up a massive protecting film. Cheap lacquers invariably lead to breakdown of the silver film.

(2) **Copper Films** may be deposited on glass by the method of F. D. Chattaway (Proc. Roy. Soc. 1907, A, **80**, 88). The coating bath is made up as follows: 9 g. of hydrazine sulphate is dissolved in 150 c.c. of distilled water and heated at 60°, and to this is added, with constant stirring, 90 c.c. of a saturated solution of copper hydroxide and ammonia at 16°, the resulting mixture being a clear yellow colour. The glass is then sponged over with the mixture, this being a most necessary step in the process. To the solution is then immediately added slowly and with constant stirring 87·5 c.c. of a solution at 60° of 11·1 g. of pure caustic potash in 100 c.c. of water. The solution should still be of a yellow colour without any precipitation taking place. The mixture is then poured into the coating vat (of copper) standing in a hot water bath at 43°, and the glass on a float at

once immersed and the float periodically rotated. The temperature of the bath is then very gradually raised to 57° over a period of about 20 minutes, for the first 15 of which the bath turns a dark green colour before finally acquiring a pink shade. After a further 5 minutes the film is thickened by the addition of a mixture of 50 c.c. of the copper hydroxide-ammonia solution at 16° with 10 c.c. of the potash at 60°, the temperature of the bath being lowered to 43° before the addition. The float is removed while adding this and stirring the mixture, and is quickly replaced and the same heating schedule followed. Further reinforcements of the coat can be obtained by repetitions of the above treatments and by electroplating from a bath made by boiling 1 part of potassium bitartrate with 10 parts by weight of water and adding as much hydrated copper carbonate as will dissolve. A safe current density is 0·25 amp. per sq. dcm., heavier currents tending to cause stripping of the film. The ordinary acid or cyanide plating baths are useless.

(3) *Dark Coloured Mirrors.*—Lead sulphide films may be prepared (O. Hauser and E. Biesalski, Chem.-Ztg., 1910, **34**, 1079) as follows: The glass plate is supported in a developing dish on four blocks of paraffin wax at the corners, and a solution of 1 gm. thiourea in 50–75 ml. water is poured over followed by 50–70 ml. of dilute lead acetate solution and 25 ml. of dilute caustic potash or ammonia solution, with continuous rocking to mix the solution. The white lead hydroxide darkens to sulphide and in about half an hour the metallic sulphide film forms first on the lower and then on the upper surface of the plate, that on the lower surface being the best.

(4) **Sputtered Films** of platinum group metals, or of gold, silver, copper and lead, may be produced by discharge from a cathode of the metal in hydrogen at such a pressure that the "dark space" just reaches the support on which the mirror is to be produced.

(5) **Evaporated Films.** — By volatilising metals in a tungsten or other suitable electrically heated spiral *in vacuo* (0·001 mm. Hg and lower), films of very satisfactory reflecting characteristics have been built up. Aluminium in particular has proved promising, though the producers of precious metal urge the claims of rhodium (M. Auwärter, J. Appl. Physics, 1939, **10**, 705).

(6) **Heavier Metallic Films** are produced on glass by spraying, *e.g.* with the Schoop gun, molten aluminium through a stencil on to a hot glass surface. This is applied to toughened glass articles to produce heating grilles on glass. B. Long (J. Soc. Glass Tech. 1937, **21**, 428) describes a panel of "*Securit*" glass 50 × 40 cm. with a Greek fret of 30 strips, 45 × 1 cm. consuming approximately 500 watts to give a surface glass temperature of 130°C. Lower ratings are applied to glass blocks for flooring, a few watts per square decimeter being sufficient to give a temperature of 30–40°C. on the non-metallised glass surface. The adhesion of sprayed aluminium to glass is very marked, a force of more than 150 kg. being needed to separate test-pieces of glass 4 × 2 × 2 cm. joined end to end by a circular soldered region 1 sq. cm. in area. This metal is largely used to join together the two halves of which hollow glass building blocks are composed (*see* p. 595*a*).

(7) **Iridescent Glass,** which in antique specimens is produced by surface decay, is obtained artificially by the action of metallic vapours. After being made at the furnace and while still red hot, therefore, the article is rotated rapidly inside an iron box or oven in which suitable metallic salts are volatilised. Various mixtures of salts are employed, such as: (1) stannous chloride 90 parts, strontium nitrate 5, barium chloride 5; (2) stannous chloride 90 parts, barium chloride 2, bismuth nitrate 5. The bright iridescent coating may be made matt by reheating several times in the mouth of the furnace. The iridescence may be greatly varied, as in Tiffany glass, by treating coloured glasses or those with patterns. Brilliant metallic effects may be obtained by adding a silver or a bismuth salt to the glass batch and reheating the object, before iridising, in a reducing flame whereby a metallic surface deposit is produced.

Alternatively a spray of $FeCl_3$ 2·5 g., $SnCl_2$ 350 g., $Sr(NO_3)_2$ 150 g., HCl 5,000 ml. is made up on the sand bath, filtered through linen after standing, and is used in a simple type of spray with air at 15 lb. per sq. in. to coat the hot glassware in a small chamber ventilated to remove the poisonous metallic vapours (T. Siroky, Sprechsaal, 1928, **61**, 1004). If no gold tone is needed, the iron salt is omitted.

(8) **Lustres** of metals, in particular of the platinum group and gold, are made by dissolving the metallic salt in so-called sulphur balsam, prepared from sulphur, Venice turpentine and turpentine oil with or without rosin (colophony). In the case of bismuth salts, however, no sulphur is permissible or black tones are produced. The metallic "resinates" obtained are made up in essential oils, *e.g.* sassafras, lavender, rosemary, fennel, etc., and are applied mixed with asphalt solution by spraying or painting. One recipe for a 6% solution of liquid platinum specifies 500 g. Pt-containing resin, 250 rosemary oil, 150 fennel oil, mix and add 14 g. rhodium solution, 6 g. chromium solution, 70 g. bismuth solution and 10 g. colophony. Thin with asphalt and colophony solution in ratio 1:2 if a 4% Pt solution is needed (F. Chemnitius, *ibid.* 1927, **60**, 182, 226, 313).

Staining is carried out by using either silver or copper compounds. B. W. Müller is said to have been the first to use $AgCl$ for silver staining. The $AgCl$ or Ag_2O mixed with 5 times its weight of ochre is ground with turpentine (sometimes dammar is also added) and is painted on the glass, which is then fired in a muffle furnace to 600–650°C. The removal of the residual ochre mixture leaves a yellow stain on the glass. Presence of oxides of iron and arsenic or antimony are said to favour colour development as does a smoky (reducing) atmosphere. Copper staining was developed by F. Egermann in Haida in 1832 (L. Springer, "Die Glasmalerei u. Aetzerei," p. 79, 1923). Four parts CuO and three of ochre are ground together with vehicle and painted on the glass which, in the case of a glass of composition SiO_2 72, Fe_2O_3

and Al_2O_3 0·3, CaO 9, Na_2O 0·55, K_2O 12, is subjected to three firings, first in an oxidising atmosphere, which gives a blue green colour to the glass visible when the excess paste is washed off. After cleaning, the glass is put through the second or reducing fire, carbonaceous matter being set in the muffle which is lightly sealed. After cooling and removing most of the adherent carbon the glass is again heated and the black stain burnt out to leave the red colour. P. Gilard and L. Dubrul (J. Soc. Glass Tech. 1937, **21**, 238) state that the principal glass components have a greater influence than in the case of silver staining. Potash glasses are better than soda ones, zinc and magnesium oxides appear to act as stabilisers and As_2O_3, SnO, CaF_2, FeO and C appear to be favourable.

ENAMELLING PROCESSES.

(*a*) **Dusting on Process.**—A few drops of lithographic varnish are rolled out on a flat plate by a roller squeegee so that the latter becomes uniformly coated. It is then rolled over a rubber template bearing the design, and the bottle or other article to be decorated is in turn rolled over this on guides so that an imprint of the design in varnish is taken on the desired place. Powdered enamel colour is then sprinkled on and the excess dusted off with a soft mop or pad of wool. The bottles then pass to the enamelling lehr where the design is fused on to the glass.

(*b*) **The Transfer Process.**—A design printed in ceramic colour is held between a film of cellulose material ("*Cellophane*") and a sheet of paper which is coated on the side next the design with a substance readily softened by, and soluble in, water. The transfer is floated on warm water cellophane side up, the paper backing falls away in a few seconds, leaving the cellophane still floating with the design on the under surface. The bottle or other article to be decorated is carefully immersed in the water so that no air bubbles adhere to its surface, and is brought up below the transfer so that the latter, on gently raising the bottle from the water, adheres to it in correct register and without any air bubbles included. After drying, the bottles are passed through an enamelling lehr or muffle. Alternatively a design may be transferred from an engraved plate by transfer paper using dry enamel powder mixed with lithographic varnish, etc.

(*c*) **The Screen Process.**—A stencil of the design is prepared either by cutting or by photographic means, and is attached to the underside of a fine silk screen held in a frame. Ceramic colour is forced through the screen and stencil by means of a squeegee on to the ware, which is supported a little below ($\frac{1}{16}$–$\frac{3}{16}$ in.) the screen so that the latter only makes contact as it is depressed by the squeegee thus giving a clean and not a smudged outline. It is claimed that a much heavier application of colour may be made by this process.

Glass Painting is carried out by the various colouring oxides and compounds elsewhere described in this article. They are mixed with a suitable flux in which they may or may not dissolve. In the former case, when applied to glass, the painting is transparent, unless specially rendered opaque as by the addition of stannic oxide, whilst in the latter it is non-transparent. The flux for gold purple is obtained by melting a mixture of quartz 4 parts, red lead 3, borax 6; for other colours, a flux made from quartz 2, red lead 6–9, borax 1, may be employed. The mixture of the colouring materials finely ground and thoroughly mixed may be used directly for painting, or it may first of all be sintered or fritted, and again finely powdered. In either case the fine powder is thoroughly ground with turpentine or other oil as medium, applied with a brush to the glass, and the latter then heated in a muffle furnace to a temperature sufficient (about 800°C.) for the thorough fusion of the flux and colour to a brilliant surface. Slow cooling down is then desirable. The vitreous paints so applied should, for successful burning-in, have a coefficient of expansion not greatly different from that of the glass treated.

Glass Beads and Artificial Gems.—Glass beads are made from previously drawn tubing of varying diameter and bore, and of various colours. The tubing is next cut into lengths suitable for the size of the bead. If the latter is to be cylindrical, the beads may be made at the lamp by merely softening the cut ends to round off the edges. For spherical beads, the cut lengths are kneaded in moist clay, or clay and ground charcoal, to prevent collapse of the walls during subsequent heating. The heating is carried out in a revolving drum, to redness, whereby the rounded shape is given and the edges melted. Alternatively a thread of glass from a rod softened by heat is wound around a steel wire (coated with a thin wash of refractory clay) until a bead is built up. This and others similarly made are drawn off the wire when cold. In another process hot glass rod is pinched by tongs between moulds to form various shapes, *e.g.* to simulate cut decoration.

The thin-walled spherical beads are made by blowing thin bulbs and either filling them with wax or coating them internally with "essence of pearl," consisting of ground fish scales in ammonium chloride. The second method produces the pearl beads. (For method of applying the pearl coating, *see* O. Parkert, Sprechsaal, 1919, **52**, 23, 191.)

Artificial gems are made by adding suitable colouring material to a glass with high lead content, and therefore of high refractive index and brilliance when cut. The colourless paste, or *strass*, may be made from sand 100 parts, red lead 150, potash 30, the materials being of high quality. The resulting glass may be ladled into water and subsequently re-melted to obtain homogeneity and then ground for admixture with the colouring agent. *Rubies* may be prepared from 1,000 strass, 1 Purple of Cassius, 5 stannous oxide, 10 antimony oxide; *emeralds* from 1,000 strass, 1 green chromium oxide, 8 cupric oxide; *amethysts* 1,000 strass, 8 manganese dioxide, 2 cobalt oxide. The strass and colouring matter must be made homogeneous by fusion using small porcelain pots holding up to 50 lb. glass. (*v.* Gems, Imitation and Counterfeit.)

Quartz Glass.—Whilst ordinary glasses are produced by the fusion of basic oxides with silica and in some bases boric oxide, it must be borne in mind that the use of such basic oxides is primarily to permit fusion to take place at the temperatures at present commercially attainable. Silica in itself possesses so many valuable properties that if it could be fused readily it would displace many types of glass. The high temperature of fusion restricts the scale on which melting can be carried out, but already, silica ware has become a recognised article of commerce, being worked into tubing, rod, beakers, flasks, crucibles and other types of scientific apparatus, quartz threads for galvanometric mirror suspensions, nitric acid stills, sulphuric acid condensation plant and chimneys for incandescent lamps.

Two types of fused silica ware are on the market, the transparent, made from quartz, and the opaque or translucent, produced from sand or crushed quartz. The *transparent* form is worked in the oxy-hydrogen flame, and the size of the article capable of being made is restricted to small crucibles and dishes, and the smaller sizes of flasks, beakers and similar articles. The *non-transparent* silica can now be worked in masses up to 200 lb., and tubes 4 in. or more in diameter form a stock article. The starting point for tubes is a hollow core of plastic silica produced by fusing a mass of white sand round a central core electrically heated, the core being removed when the cylinder has been formed and drawn into tubing in the ordinary way. In the plastic condition such a silica cylinder can be drawn into lengths of 90 or 100 ft. The rough outer surface of the tube may be ground down or it may be glazed either electrically or by an oxy-hydrogen flame.

For articles other than tubing, the cylinder is closed at one end and blown in a mould by compressed air.

The temperature required for fusing and working the sand is 1,800–2,000°C. As only a plastic and not a completely fused condition is reached, the fine air bubbles are not removed, and reflection from them gives rise to the silky, lustrous appearance characteristic of this type of fused silica. (*See* F. Bottomley, J.S.C.I. 1917, **36**, 577.)

In a process patented by H. P. Hood, M. E. Nordberg and Corning Glass Works (B.P. 442526, 8.8.34) articles made from the glass SiO_2 75, Na_2O 5, B_2O_3 25, are maintained at 525–650°C. for periods of from a few hours to a few days until the glass separates into a silica rich phase and one containing practically all the alkali and boric oxide. Immersion in a bath of acid removes the latter, leaving a skeleton of substantially pure silica which after washing in running water is heated to give a high silica glass. There is a very large shrinkage in this last operation.

Quartz glass has an extremely small coefficient of linear thermal expansion, namely, $5{\cdot}2 \times 10^{-8}$, and articles made from it can be heated to redness and quenched in cold water without fracture. Hence its value for heat-resisting glassware. Unfortunately, fused silica ware cannot be maintained for any considerable period at temperatures higher than 1,000°C. owing to its tendency to revert to the crystalline form stable at such temperature, namely, tridymite, when the article is liable to break down.

Fused silica is practically unacted on by water, and all acids except hydrofluoric acid, and phosphoric acid above 400°C. It is, accordingly, of very great value in precise chemical analysis where water, neutral salt solutions and acids are alone concerned. Further, as a consequence of its resistance to solubility by water, and its non-hygroscopic character, fused silica is a very good electrical insulator. As an acid material itself, it is naturally attacked by the alkalis, and the use of silica crucibles is therefore much restricted since they cannot be used for fusion of metallic oxides.

Transparent quartz is transparent to ultraviolet light and on this account finds special use in the form of plates, lenses, and wedges or prisms in optical apparatus, and in mercury vapour lamps. The refractive index for the D-line is 1·45847, and the dispersion constant γ 67·92 (Gifford and Shenstone, Proc. Roy. Soc. 1904, **73**, 201).

M. P.
W. E. S. T.

GLASS OF ANTIMONY (*v.* Vol. I, 447*b*).

GLASS OR GOLD FLUX (*v.* Vol. I, 559*d*).

GLASS, OPTICAL. The primary requirement of optical glass is that it shall be homogeneous and isotropic.

In the manufacture of ordinary commercial glass the raw materials, sand, limestone, etc., are mixed thoroughly together before they are melted, but no mixing other than that produced by convection currents and diffusion is attempted during founding. As a result, minor variations of refractive index due to small variations of composition are unavoidable, so that an object seen through a plane parallel-sided piece of ordinary glass might be expected to appear more or less distorted. In general, however, the methods of manufacture cause the different portions of the glass to be spread in layers which lie substantially parallel to the surface, and when the glass is looked through normally this distribution largely or entirely masks the effects of variation of refractive index. Unless the glass is accurately plane parallel also, the distortion produced by variations of thickness is of such comparatively large magnitude that effects due to variations of refractive index pass unnoticed.

How large those effects could be is easily seen, however, by looking edgewise through a narrow strip of plate glass which, when looked through in the ordinary way, produces no distortion. When viewed edgewise the glass can be seen to consist of an enormous number of layers, all differing slightly in refractive index, and nothing can be seen clearly through it if the strip is more than 1 or 2 in. wide.

The uses to which optical glass is put require that perfect image-formation shall be possible irrespective of the direction along which light passes through the glass. For *thin* lenses a striated or stratified glass, such as plate glass, may not be entirely unsatisfactory if the image-forming rays pass substantially normal to the surface and through only small areas, as in spectacle lenses. For wide-aperture and wide-angle lenses, however, the glass used must be of uniform refractive index throughout if perfect images are to be obtained. In prisms, also, uniformity of refractive index is essential, since the light rays pass in different directions through different parts of the prisms and, not infrequently, may pass successively in different directions through the same part of the glass.

To obtain the necessary high degree of homogeneity, optical glass is stirred mechanically after the ingredients have all been completely melted, and this stirring is continued for a period of several hours as the glass cools, until the viscosity is so high that further mixing is virtually impossible. By stirring in this way not only are the original ingredients distributed uniformly throughout the melt, but also any pot material dissolved by the glass during melting is distributed and given every possible opportunity of becoming uniformly disseminated. After stirring, the glass is not gathered, ladled, poured or worked in any way as in making ordinary glass articles or flat glass, but is allowed to cool down in the pot at a rate which will cause the glass to break into lumps of convenient sizes as it cools. These lumps are then reheated and moulded into standard plates or into rough prism and lens forms, after which they are annealed under conditions which minimise temperature gradients in the glass during final cooling.

The stirring and the practice of allowing the glass to cool undisturbed in the pot are the only essential features distinguishing optical glass manufacture from the methods of manufacture used in making commercial glasses. It is true that, for most purposes, optical glasses should be colourless and highly transparent, and that their optical properties are required to lie within close limits of some specified value. These objects are achieved by using ingredients in which impurities are not present in sufficient amount to produce colour or to cause significant changes of refractive index. The term " Optical Glass " must, however, be accepted as including glass, whether coloured or not, which is rendered homogeneous by stirring, as, for example, special neutral or coloured glasses such as are incorporated in certain types of optical apparatus or as the high-quality " haze-cutting" colour screens used in conjunction with wide-aperture photographic lenses.

At one time the needs of the optical-glass industry could be reasonably satisfied by a comparatively small number of types of optical glass, since achromatic lenses of comparatively small angle represented the limits to which lens-design had developed, and such lenses can be made up from almost any two glasses which differ sufficiently in refractive index. The need for special types of glasses came to be recognised when lenses of high-aperture, particularly microscope lenses, came to be designed. Faraday had made and studied the properties of a considerable number of glasses containing previously unused ingredients, such as barium oxide and boric anhydride or borates, and also containing the more usual ingredients such as lead oxide in unusually large proportions. W. Vernon Harcourt and John Hopkinson had also worked on similar lines, the latter in association with Chance Brothers, between 1872 and 1877. Their work had, however, aroused little outside interest, and in the absence of any demand, these special glasses had not been manufactured in any quantity. The commercial development of glasses of special types was eventually undertaken by Schott, who, at the instigation of Abbe, devised and began to produce commercially a number of glasses having the particular properties which Abbe found would be of assistance in the production of microscope objectives of high numerical aperture.

The number of types of optical glass eventually introduced was of the order of 75–100, though several of these were unsuitable on grounds of insufficient durability, and have since gone out of use. It has also been shown that, with improved methods of lens computation, a proportion of the remaining types could also be dispensed with, if necessary.

Optical glasses are classified broadly into crowns and flints according to the value of the reciprocal of their dispersive powers for the range of spectrum between the C and F lines,

$$\frac{n_D - 1}{n_F - n_C}.$$

This quantity is usually referred to as the ν-value, but is commonly printed as the V-value.

Optical Glasses.

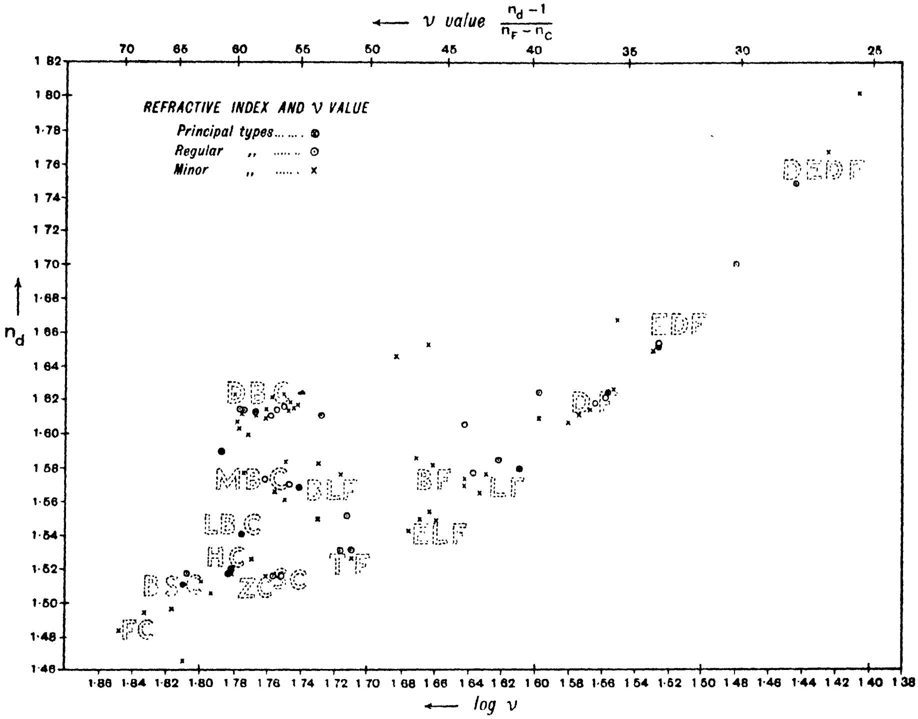
Type.	SiO_2	B_2O_3	Al_2O_3	PbO	CaO	ZnO	BaO	Na_2O	K_2O	F_2	P_2O_5	MgO	Optical constants.	
													ν.	n_D.
Phosphate crown .		3·0	10·0						12·0		70·5	4·0	70·0	1·516
Fluor crown . . .	53·3	16·2	8·8						16·2	5·3			67·2	1·471
Borosilicate crown .	70·4	7·5			2·0			5·3	14·5				63·4	1·510
Hard crown . . .	74·6				5·0			9·0	11·0				60·2	1·501
Medium barium crown	59·5	3·0				5·0	19·2	3·0	10·0				59·6	1·541
Dense barium crown.	39·5	6·5	2·5			9·0	42·0						56·7	1·610
Light barium flint .	51·7			10·0		7·0	20·0	1·5	9·5				50·4	1·572
Extra light flint . .	62·7			23·9				4·5	8·3				46·9	1·541
Light flint . . .	53·3	0·8		33·5				4·0	8·0				41·0	1·580
Dense flint . . .	46·1			45·1				1·7	6·8				36·6	1·616
Extra dense flint .	34·7			61·0				1·5	2·5				29·5	1·717
Double extra dense flint	21·0			79·0									20·9	1·923

The distinction between crowns and flints is an arbitrary one, glasses having ν-values of 55 and upwards being classed as crowns, while a glass with a ν-value lower than 55 is classed as a flint.

In plain soda-lime and lead glasses the dispersive power increases in a fairly regular manner with the mean refractive index (or the refractive index for the D lines), *i.e.* a high refractive index is associated with a low ν-value. In glasses containing a notable proportion of barium, however, high refractive indices are associated with relatively low dispersive powers, a property which renders the barium glasses of particular importance to the optical designer.

Some idea of the range of compositions used in optical glass manufacture can be obtained from the table, which gives approximate values of the principal oxide contents of glasses belonging to the main type-groups. The full range of optical properties is indicated in the figure by the initial letters of the glasses. For the majority of the glasses the points representing the optical properties lie reasonably close to a smooth curve, but for glasses containing barium the corresponding points lie above this curve, by amounts which increase as the proportion of barium in the glass increases.

H. M.



GLASS, REINFORCED, TOUGHENED AND SAFETY.

Brittleness has militated against the use of glass in many applications for which, otherwise, it would be the ideal material. This disadvantage must be accepted, however, along with any associated risks, in circumstances where translucency or transparency combined with screening against weather or other disturbance are essential and the object of any reinforcement, toughening process or lamination is to reduce these risks to a minimum.

In considering the glasses specially made or specially treated to minimise these risks it will be convenient to deal also with the non-brittle and flexible transparent plastics now available, which can be used in place of glass.

Reinforced Glass (Wired Glass).—Wired glass is the only truly "reinforced" glass. It is simply a sandwich made by feeding a strip of hexagon-mesh or square-mesh wire netting between two layers of glass as the glass passes through the rolling machine, the whole being finally rolled so as to weld the two layers of glass together with the wire between them.

The advantage of wired glass over ordinary glass is not that it offers any greater resistance to cracking under flexure or impact, but that when it is cracked or even shattered the pieces are strongly held together by the embedded wire. The risks of damage due to falling glass or to flying splinters are thus very greatly reduced by the use of wired glass in place of ordinary glass, particularly in roof-glazing or under conditions in which there is risk of the glass being exposed to severe blows or to blast-waves from explosions.

Toughened Glass.—Rupture of glass, as of all other materials, occurs only when some part is put into excessive tension. Glass is much weaker in its surface layers than in its interior layers, consequently any process which will increase the *effective* tensile strength of the surface layers will also render the glass less liable to break under impact or under steady loads.

Toughening consists in heating glass to a temperature just high enough to cause incipient softening, then chilling the glass rapidly. The surface layers thus become rigid while the interior is still slightly soft, and the glass cools under conditions which maintain a considerable difference of temperature between the interior and the surface layers until the whole of the glass has cooled well below the softening point.

Glass " toughened " in this way is in a state of severe strain ; the surface layers and layers lying close to the surfaces are in considerable compression, and this system of compressions is balanced by tensile strains distributed through the more central layers, the maximum tension occurring in the middle of the glass. When such glass is deformed by flexure or impact no part of the surface can be put into true tension until it has been stretched by an amount sufficient to neutralise the compression strains in the surface layers. Toughened glass is thus stronger than glass which has been annealed in the usual way, since it will withstand much greater deformation and correspondingly larger mechanical forces without fracture.

Toughened glass of ordinary composition will also withstand the strains set up by thermal gradients or thermal shocks which would cause rupture if the glass were annealed, and in this respect it rivals the special low-expansion or heat-resisting glasses. The heat-resisting properties of low-expansion glasses can, of course, be increased by toughening, and this has been applied to the production of certain types of glass cooking-ware which can be used directly over the flame of an ordinary cooking-stove.

Safety Glasses.—The property required of " safety glasses " for land-transport vehicles is that " when broken they shall not fly into fragments capable of causing severe cuts." For particular purposes, also, protective glasses may be required to provide clear vision combined with protection as, for example, in observing processes which involve danger of explosion or, in certain cases, to provide protection against bullets. These glasses include toughened and laminated glasses, and also transparent plastics commonly described as " organic " glasses.

(*a*) *Toughened Safety Glass.*—The " safety " properties of toughened glass are attributable primarily to the fact that glass which is toughened to the proper degree disintegrates into small fragments when broken, no fragment being large enough to cause more than a comparatively light scratch. The strength of toughened glass as compared with ordinary glass is an added advantage from the " safety " point of view, since it reduces risk of fracture ; it is, however, regarded as of secondary importance compared with the fine fragmentation which occurs if the glass should be broken.

(*b*) *Laminated Safety Glass.*—Ordinary laminated glass consists of two sheets of glass strongly bonded together by means of a flexible transparent interlayer. When such an assembly is broken by a heavy blow both the glasses may be shattered, but if the interlayer is tough and the adhesion satisfactory, risk of injury due to flying glass splinters is avoided.

Laminated screens affording a very high measure of protection may be built up of several layers of glass of suitable thicknesses alternating with and bonded together by flexible transparent materials. A bullet-proof assembly can, for example, be built up in this way, the total thickness necessary being not more than 2¼–2½ in. For certain purposes, also, toughened plates of glass may be bonded together with flexible transparent interlayers.

Interlayer materials used are of various types, the more usual ones at the present time being cellulose nitrate and cellulose acetate. The polyvinyl acetate resins in sheet form are, however, coming increasingly into use and are particularly suitable on account of their high adhesive properties and their great extensibility or " toughness." (*v.* Vol. I, 90*c*).

(*c*) *Organic Safety Glasses.*- Flexible transparent organic materials in sheet form are used as " safety glasses " in place of glass screens or windows, where lightness, rigidity and non-splintering properties are all essential. The cellulose esters were the earliest organic materials which could be used in this way, but more suitable organic products are now available among the acrylic resins, and the polystyrenes.

By comparison with glass these materials are at a commercial disadvantage as regards cost. They are also much softer than glass and, in consequence, are more liable to scratching and other surface damage. Their lightness and toughness make them specially suitable, however, for use as windshields, cockpit covers, saloon windows and other transparent fittings in civil and military aircraft, and the organic safety glasses have come into considerable use in these and similar applications.

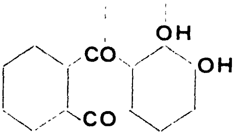
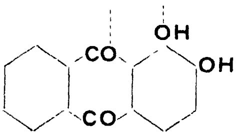
H. M.

END OF THE FIFTH VOLUME.

ADDENDUM.

Food Preservatives.—Since this article was written the Ministry of Food has permitted the use of Boric Acid to a limited extent. S. R. & O. 1940, Nos. 547, 982.

ERRATA.

Vol.	*Page*	*Line*	*For*	*Read*
I	v	5*	etalia J. C. S., 1934 1022	*and others* J. C. S., 1934, 1016–1039
I	1*c*	22	Erganzungsband	Ergänzungsband
I	142*d*	32*	N=C—N | ||	N=CH—N | ||
I	692*d*	34*	*Locanthus*	*Loranthus*
II	25*a* 25*c*	30 24	Thénard	Thenard
II.	52*a*	17	Ardnt	Arndt
II	288*c*	10	2-deoxypentoses	two deoxypentoses
II	320*c*	14	Hexabrooethane	Hexabromoethane
II	361*a*	11 and 12	Two varieties of carborundum articles are made: *Refrax* . . .	Among the carborundum articles made by the Carborundum Company are: "*Refrax*" . . .
II	361*a*	15	*Carbofrax*	"*Carbofrax*"
II	381*c*	16 and 19	*Kombe*	*Kombé*
II	432*d*	23*	Schimdt	Schmidt
II	464*d*	33*	Acetycellulose	Acetylcellulose
II	711*b*	2*	*ter*-butyl	*tert*-butyl
III	107*a*	18	on cooling a	on cooling. A
III	107*b*	19*	Verdian	Veridian
III	107*b*	21*	Academische	Akademischer
III	293*d*	8*	whose	his
III	335*d*	formula III		
IV	xv	23	*Glasshütte* Glasshutte	*Glashütte* Glashütte

* from bottom

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PHARMACEUTICS